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LOWER BOUNDS TO ENERGY EIGENVALUES BY THE PARTITIONING TECHNIQUE

by

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Dedicated to my
Beloved Mother

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CHAPTER I

INTRODUCTION

Although one cannot expect exact solutions for a given quantum mechanical eigenvalue problem, it is often possible to find upper and lower bounds to the eigenvalues. Upper bounds can be obtained satisfactorily by the well-known variational calculations, for example, Rayleigh-Ritz procedures[1,2]; however, in order to estimate the accuracy, the knowledge of lower bounds is essential.

The problem of finding lower bounds has been approached in many different ways. Among those, the intermediate problems originated by A. Weinstein[3] and extended and developed by Aronszajn[4] have been widely used. Many fundamental problems in quantum theory have been studied by Bazley and Fox[5] using these intermediate problems.

Recently P. O. Löwdin has developed a new method[6,7] for the study of lower bounds to energy eigenvalues by the use of the partitioning technique[8]. In the partitioning technique, the first order iteration procedure $\mathcal{E}_{k+1} = f(\mathcal{E}_k)$ brackets at least one true eigenvalue E. By means of an "inner projection"[6] on a finite manifold in the Hilbert Space, one can evaluate lower bounds to any desired accuracy. For a Hamiltonian of the form $\mathcal{H} = \mathcal{H}^0 + V$, where V is positive definite, one may consider the intermediate Hamiltonians:

$$\mathcal{H}(n) = \mathcal{H}^0 + V^{\frac{1}{2}} Q^n V^{\frac{1}{2}}$$

where Q^n is a Hermitian projection operator for an arbitrary subspace of order n, which for $n \to \infty$ converges towards the identity operator[4,9].

In the first part of this dissertation, we develop the theoretical foundations of our approach through the partitioning technique extended to a multi-dimensional reference manifold.

In the last part, we apply these procedures to the Stark effect in the rigid rotator as an example of a one-dimensional reference manifold and to the two-electron isoelectronic series as an example of a multi-dimensional reference manifold.

CHAPTER II

VARIATION PRINCIPLE AND SEPARATION THEOREM

For a Hamiltonian operator $\mathcal{H}$ which is bounded from below, a variational calculation gives an upper bound to the ground state eigenvalue of $\mathcal{H}$. The variation principle states $\delta \langle \mathcal{H} \rangle_{AV} = 0$, where $\langle \mathcal{H} \rangle_{AV}$ is the expectation value of the operator $\mathcal{H}$:

$$\langle \mathcal{H} \rangle_{AV} = \frac{\int \Psi^* \mathcal{H} \Psi (dx)}{\int \Psi^* \Psi (dx)} \equiv \frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = E \quad . \tag{2.1}$$

Let us consider that the trial function Ψ is expanded in terms of a complete set of functions $\{\phi\} \equiv \{\phi_1, \phi_2, \ldots\}$, which has the overlap matrix Δ with the elements

$$\Delta_{ij} = \int \phi_i^* \phi_j (dx) \quad . \tag{2.2}$$

The Hamiltonian is then represented by a matrix $\|\mathcal{H}\|$ with the elements

$$\mathcal{H}_{ij} = \int \phi_i^* \mathcal{H} \phi_j (dx) \quad . \tag{2.3}$$

In practical calculations the complete set $\{\phi\}$ has to be truncated to a set $\{\phi\}_n \equiv \{\phi_1, \phi_2, \ldots, \phi_n\}$ of a finite order, say order n, so that

$$\Psi = \sum_{i=1}^{n} C_i \phi_i \quad . \tag{2.4}$$

In order to improve our expectation value using this finite discrete

set, we invoke the variation theorem. For an expectation value of an operator bounded from below, this variational technique gives an upper bound to the eigenvalue of the ground state. Upper bounds to the excited states are estimated through Rayleigh-Ritz process by the expansion of the trial function in the form of (2.4).

Denoting the column vector of coefficient C_i by C, and the adjoint of C by $C^{\dagger}$ [*1], one can write an equivalent equation to (2.1) in terms of matrix notation

$$\langle \mathcal{H} \rangle_{AV} = C^{+} H C / C^{+} \Delta C = E. \qquad (2.5)$$

Varying the coefficients C_i and applying the variation principle, one obtains

$$\sum_j (\mathcal{H}_{ij} - E \Delta_{ij}) C_j = 0, \quad (i=1,2,\ldots,n) . \qquad (2.6)$$

The roots $E_1, E_2, \ldots, E_n$ of the associated secular equation

$$\det (\mathcal{H}_{ij} - E \Delta_{ij}) = 0 \qquad (2.7)$$

give the upper bounds to the n lowest eigenvalues of $\mathcal{H}$ in order[6,10,11].

If we introduce a projection operator $\mathcal{O}^n$ associated with the truncated set $\{\phi\}_n$, such that

$$\mathcal{O}^n \phi_i = \phi_i , \qquad (i=1,2,\ldots,n), \qquad (2.8)$$

and characterized by the relations

$$\mathcal{O}^n \mathcal{O}^n = \mathcal{O}^n, \quad \mathcal{O}^{n\dagger} = \mathcal{O}^n \text{ and } Tr(\mathcal{O}^n) = n. \qquad (2.9)$$

[*1] The symbol † applied as a superscript to an operator or to a matrix denotes its Hermitian adjoint.

then $\mathcal{H}^n$ defined by

$$\mathcal{H}^n \equiv \mathcal{O}^n \mathcal{H} \mathcal{O}^n \tag{2.10}$$

gives eigenvalues E_1, E_2, ..., and E_n, which are equal to the roots of the secular equation (2.6). Hence (2.6) can be replaced by an eigenvalue equation of the form

$$\mathcal{H}^n U_i = E_i \mathcal{O}^n U_i, \qquad (i=1,2,\ldots,n), \tag{2.11}$$

with

$$\mathcal{O}^n U_i = U_i .$$

Since

$$\mathcal{H}^n \mathcal{O}^n = \mathcal{O}^n \mathcal{H}^n , \tag{2.12}$$

it is possible to diagonalize the $\mathcal{H}$ and Δ matrices simultaneously by a unitary transformation which leaves the roots of (2.7) unchanged. Therefore any theorem or property related with the roots of (2.7) does not depend on the choice of the basis as long as the basis spans the same space. Let us further introduce an additional function ϕ_{n+1} to the truncated set $\{\phi\}_n$, so that $\{\phi\}_{n+1} \equiv \{\phi_1, \phi_2, \ldots, \phi_n, \phi_{n+1}\}$ and an associated Hermitian projection operator $\mathcal{O}^{n+1}$ characterized by the relations

$$\mathcal{O}^{n+1}\mathcal{O}^{n+1} = \mathcal{O}^{n+1}, \quad \mathcal{O}^{n+1\dagger} = \mathcal{O}^{n+1}, \quad \mathrm{Tr}(\mathcal{O}^{n+1}) = n+1, \tag{2.13}$$

$$\mathcal{O}^{n+1}\mathcal{O}^{n} = \mathcal{O}^{n}\mathcal{O}^{n+1} = \mathcal{O}^{n} \quad \text{and} \quad \mathcal{O}^{n+1}\phi_{n+1} = \phi_{n+1}.$$

Then $\mathcal{H}^{n+1}$ defined by

$$\mathcal{H}^{n+1} = \mathcal{O}^{n+1} \mathcal{H} \mathcal{O}^{n+1} \tag{2.14}$$

will have n+1 eigenvalues. For the simplicity of notation, we will sometimes use m for n+1 in this chapter.

It is interesting to see how these upper bounds given by the variation principle are improved by enlarging the subspace in which the trial function Ψ is varied. This effect is qualitatively explained by the well-known "separation theorem"[10,11], which states that the n eigenvalues of $\mathcal{H}^n$ are upper bounds to the n eigenvalues of $\mathcal{H}$ in order from below, and the eigenvalues of $\mathcal{H}^n$ and $\mathcal{H}^m$ satisfy the following inequality:

$$E_1 \leq h_1 \leq E_2 \leq \ldots \leq E_n \leq h_n \leq E_{n+1} , \qquad (2.15)$$

where h_i denotes the n eigenvalues of $\mathcal{H}^n$ and E_i denotes the n+1 eigenvalues of $\mathcal{H}^{n+1}$.

Let us now study the separation theorem in somewhat more detail in connection with the degeneracy and the common eigenvalues of $\mathcal{H}^n$ and $\mathcal{H}^{n+1}$ since they are closely related to the asymptotic behavior and the lost eigenvalues in the partitioning technique[8,12].

In the following, for simplicity, we will work with the orthonormal set of $\{\phi\}_m$.

Let us consider a matrix H^m with the matrix elements of the form

$$\mathcal{H}_{ij} = \langle \phi_i | \mathcal{H} | \phi_j \rangle , \qquad (i,j=1,2,\ldots n,m) ,$$

and transform the matrix H^m by means of the unitary transformation :

$$\begin{pmatrix} 1 & 0 \\ 0 & U \end{pmatrix} , \qquad (2.16)$$

where $\mathbb{U}$ is the n-dimensional unitary matrix consisting of eigenvectors of $\mathbb{H}^n$. Then we obtain a secular equation of the form: *2

$$\begin{vmatrix} \mathcal{H}_{mm}-E & V_{m1} & V_{m2} & \cdots & V_{mn} \\ V_{1m} & h_1-E & 0 & \cdots & \\ V_{2m} & 0 & h_2-E & \cdot & \\ \cdot & \cdot & & \cdot & \\ \cdot & \cdot & & & \cdot \\ \cdot & \cdot & & & \\ V_{nm} & & & & h_n-E \end{vmatrix} = 0, \qquad (2.17)$$

where

$$V_{mk} = \sum_{i=1}^{n} \mathcal{H}_{mi} U_{ik}, \qquad (k=1,2,\ldots,n),$$

and $$V_{km} = V_{mk}^{*} .$$

Denoting $$V_{mk}^2 = V_{mk}^{*} \cdot V_{mk}$$

one can express (2.17) by the form

$$(\mathcal{H}_{mm}-E) \prod_{i=1}^{n} (h_i-E) - \sum_{k=1}^{n} V_{mk}^2 \Big[\prod_{\substack{i=1 \\ (i\neq k)}}^{n} (h_i-E) \Big] = 0. \qquad (2.18)$$

Defining a continuous function $Y(\mathcal{E})$ differentiable to any order by

$$Y(\mathcal{E}) \equiv (\mathcal{H}_{mm}-\mathcal{E}) \prod_{i=1}^{n} (h_i-\mathcal{E}) - \sum_{k=1}^{n} V_{mk}^2 \Big[\prod_{\substack{i=1 \\ (i\neq k)}}^{n} (h_i-\mathcal{E}) \Big] , \qquad (2.19)$$

(2.18) states that m eigenvalues of $\mathcal{O}^m \mathcal{H} \mathcal{O}^m$ are the m roots of $Y(\mathcal{E})$:

$$Y(E) = (\mathcal{H}_{mm}-E) \prod_{i=1}^{n} (h_i-E) - \sum_{k=1}^{n} V_{mk}^2 \Big[\prod_{\substack{i=1 \\ (i\neq k)}}^{n} (h_i-E) \Big] = 0. \qquad (2.20)$$

---

*2 Compare with (5.20).

Let us assume that the eigenvalues of $\mathcal{H}^n$ are arranged in non-decreasing order

$$h_1 \leq h_2 \leq \cdots\cdots \leq h_{n-1} \leq h_n ,$$

then the behavior of the function $Y(\mathcal{E})$ is conveniently explained by considering the various possible cases.

Case (1). None of the elements V_{mk} are vanishing and all the h_i are different from one another.

In this case, from (2.20) we have

$$\begin{aligned} Y(h_1) &= -V_{m1}^2 \prod_{i=2}^{n} (h_i - h_1) \\ Y(h_2) &= -V_{m2}^2 \prod_{\substack{i=1 \\ (i\neq 2)}}^{n} (h_i - h_2) \\ &\cdots\cdots\cdots\cdots \\ Y(h_n) &= -V_{mn}^2 \prod_{i=1}^{n-1} (h_i - h_n) \end{aligned} \tag{2.21}$$

It is seen from (2.20) that $Y(h_1) < 0$, furthermore the sign of $Y(h_{i-1})$ is different from that of $Y(h_i)$. Hence, there exists at least one real root between $Y(h_{i-1})$ and $Y(h_i)$. We also note that

$$\begin{aligned} Y(-\infty) &\cong \lim_{\mathcal{E}\to-\infty} |\mathcal{H}_{mm} - \mathcal{E}| \prod_{i=1}^{n} |h_i - \mathcal{E}| > 0 \\ Y(+\infty) &\cong \lim_{\mathcal{E}\to+\infty} (-1)^m |\mathcal{H}_{mm} - \mathcal{E}| \prod_{i=1}^{n} |h_i - \mathcal{E}| \quad \begin{cases} > 0, & \text{if } m \text{ is even} \\ < 0, & \text{if } m \text{ is odd.} \end{cases} \end{aligned} \tag{2.22}$$

Since the signs of $Y(-\infty)$ and $Y(h_1)$ are different from each other, there exists at least one root which is smaller than h_1 and in like manner the different signs of $Y(h_n)$ and $Y(+\infty)$ guarantee that there

exists at least one root which is higher than h_n. Furthermore (2.19) cannot have more than m roots. The above reasoning gives the following separation theorem.

Theorem 2.1. If none of the elements of V_{mk} are zero and all of the h_i are different from one another, (2.19) has m distinct roots satisfying the inequality,

$$E_1 < h_1 < E_2 < h_2 < \ldots\ldots < E_n < h_n < E_m \quad . \tag{2.23}$$

Case 2. All of V_{mk} are nonvanishing and some of h_i are degenerate.

In order to facilitate our discussion, we will adopt the notation $h_i^{p_i}$, where the superscript p_i denotes the degree of degeneracy in the i^{th} distinct level in order from below, so that the following relations are satisfied:

$$h_1^{\,1} = h_1^{\,2} = \ldots = h_1^{\,p_1} < h_2^{\,1} = h_2^{\,2} = \ldots = h_2^{\,p_2} < \ldots < h_\ell^{\,1} = h_\ell^{\,2} = \ldots h_\ell^{\,p_\ell} \quad , \tag{2.24}$$

where

$$h_1^{\,1} = h_1, \; h_1^{\,2} = h_2, \; \ldots, \; h_1^{\,p_1} = h_{p_1}, \; h_2^{\,1} = h_{p_1+1} \; , \ldots, \tag{2.25}$$

$$\sum_{i=1}^{\ell} p_i = n \; . \tag{2.26}$$

Then (2.19) will have the form

$$Y(\mathcal{E}) = \left[\prod_{i=1}^{\ell}(h_i-\mathcal{E})^{(p_i-1)}\right]\left[\,(\mathcal{H}_{mm}-\mathcal{E})\prod_{i=1}^{\ell}(h_i-\mathcal{E}) - \sum_{k=1}^{\ell} W_{mk}^2 \left\{\prod_{\substack{i=1\\(i\neq k)}}^{\ell}(h_i^1-\mathcal{E})\right\}\right] \tag{2.27}$$

where

$$W_{mk}^2 = \sum_{j=j'}^{j''} V_{mj}^2 \tag{2.28}$$

with

$$j' = \begin{cases} 1 & \text{for } k = 1, \\ \sum_{i=1}^{k-1} P_i + 1 , & \text{for } k \geq 2, \end{cases}$$

$$j'' = \begin{cases} P_1 , & \text{for } k = 1, \\ \sum_{i=1}^{k} P_i , & \text{for } k \geq 2, \end{cases} \qquad (2.29)$$

and (2.20) takes the form

$$\prod_{i=1}^{\ell}(h_i^1-E)^{(P_i-1)}[(\mathcal{H}_{mm}-E)\prod_{i=1}^{\ell}(h_i^1-E)-\sum_{k=1}^{\ell}W_{mk}^2\left\{\prod_{\substack{i=1\\(i\neq k)}}^{\ell}(h_i^1-E)\right\}] = 0. \qquad (2.30)$$

The difference between (2.20) and (2.30) in their form is that (2.30) has an additional factor $\prod_{i=1}^{\ell}(h_i^1-\mathcal{E})^{(P_i-1)}$ and h_i^1 remains as a root of (2.27) with the degeneracy (p_i-1). We can use the same reasoning applied to (2.19) to $\overline{Y}(\mathcal{E})$:

$$\overline{Y}(\mathcal{E}) \equiv \frac{Y(\mathcal{E})}{\left\{\prod_{i=1}^{\ell}(h_i^1-\mathcal{E})^{(P_i-1)}\right\}} \qquad (2.31)$$

and obtain the separation theorem of the form

$$E_1^1 < h_1^1 = E_2^1 = \ldots = E_2^{(P_1-1)} = h_1^P < E_3^1 < \ldots < h_\ell^1 = E_{2\ell}^1 = \ldots = E_{2\ell}^{(P\ell-1)} = h_\ell^{P\ell} < E_{2\ell+1}^1 \qquad (2.32)$$

where

$$E_1 = E_1^1,\ E_2 = E_2^1,\ \ldots,\ E_{P_1} = E_2^{P_1-1},\ E_{P_1+1} = E_3^1,\ \ldots,\ \text{etc.}$$

It is seen from (2.32) that the change from $\mathcal{H}^n$ to $\mathcal{H}^m$ reduces the degeneracy of each level by one and $\mathcal{H}^m$ has non-degenerate roots between the degenerate sets.

Case (3). Some of V_{mk} are vanishing and none of the h_i are degenerate.

If an element, for example, V_{mj} is zero, we can write (2.19) and (2.20) as

$$Y(\mathcal{E}) = (h_j-\mathcal{E})\Big[(\mathcal{H}_{mm}-\mathcal{E}) \prod_{\substack{i=1\\(i\neq j)}}^{n} (h_i-\mathcal{E}) - \sum_{\substack{k=1\\(k\neq j)}}^{n} V_{mk}^2 \Big\{ \prod_{\substack{i=1\\(i\neq k, i\neq j)}}^{n} (h_i-\mathcal{E})\Big\}\Big] , \tag{2.33}$$

$$(h_j-E)\Big[(\mathcal{H}_{mm}-E) \prod_{\substack{i=1\\(i\neq j)}}^{n} (h_i-E) - \sum_{\substack{k=1\\(k\neq j)}}^{n} V_{mk}^2 \Big\{ \prod_{\substack{i=1\\(i\neq k, i\neq j)}}^{n} (h_i-E)\Big\}\Big] = 0. \tag{2.34}$$

In this case the eigenvalue h_j of $\mathcal{H}^n$ remains as an eigenvalue of $\mathcal{H}^m$. This is due to the fact that ϕ_m and $\sum_{i=1}^{n} U_{ij}^* \phi_i$ are non-interacting with respect to $\mathcal{H}$. Since

$$\overline{Y}(\mathcal{E}) = Y(\mathcal{E})/(h_j-\mathcal{E}) \tag{2.35}$$

has n distinct roots as discussed in Case (1), $Y(\mathcal{E})$ has m distinct roots if the j^{th} root of $\overline{Y}(\mathcal{E})$, which is located between h_{j-1} and h_{j+1}, is different from h_j, and the following inequalities are satisfied according to whether the j^{th} root of $\overline{Y}(\mathcal{E})$ is lower or higher than h_j:

$$E_1 < h_1 < E_2 \ldots < E_j < h_j = E_{j+1} < h_{j+1} < E_{j+2} \ldots \; h_n < E_m , \tag{2.36}$$

or

$$E_1 < h_1 < E_2 \ldots < E_j = h_j < E_{j+1} < h_{j+1} < E_{j+2} \ldots < h_n < E_m. \tag{2.37}$$

If the j^{th} root of $\overline{Y}(\mathcal{E})$ happens to equal to h_j, then one degeneracy of the level h_j is added and gives the following separation theorem :

$$E_1 < h_1 < E_2 \ldots E_{j-1} < E_j = h_j = E_{j+1} < h_{j+1} < E_{j+2} \ldots < h_n < E_m. \tag{2.38}$$

The above discussion can be extended easily to the case where more than one V_{mk} is vanishing.

Corollary 2.1: Degeneracy may be induced in the level h_j in the spectrum of $\mathcal{H}^m$ only when the corresponding V_{mj} is vanishing.

Case (4). Some V_{mk} are vanishing and the corresponding h_k is degenerate.

This is the combined case of Case (2) and Case (3) and (2.27) and (2.33) have to be considered. In connection with (2.27), we can consider two different cases; one, W^2_{mk} is vanishing, and the other, W^2_{mk} is not vanishing. If W^2_{mj} vanishes, for example, one can write (2.27) as

$$Y(\mathcal{E}) = (h_j-\mathcal{E})\Big[\prod_{i=1}^{\ell}(h_i^1-\mathcal{E})^{(P_i-1)}\Big]\Big[(\mathcal{H}_{mm}-\mathcal{E})\prod_{\substack{i=1\\(i\neq j)}}^{\ell}(h_i^1-\mathcal{E}) - \sum_{\substack{k=1\\(k\neq j)}}^{\ell} W^2_{mk}\Big\{\prod_{\substack{i=1\\(i\neq k, i\neq j)}}^{\ell}(h_i^1-\mathcal{E})\Big\}\Big] \quad , \tag{2.39}$$

and, as one has seen in the discussion of (2.33), degeneracy for the level h_k^1 will remain and may be increased by one through the change from $\mathcal{H}^n$ to $\mathcal{H}^m$; and if W^2_{mk} is not vanishing, then one can go back to (2.27) and it reduces to the Case (2).

The four cases discussed above give a lucid look at the separation theorem in connection with the degeneracy.

Since (2.39) is a special form of (2.27) or (2.33), in Chapter III we will not consider (2.39) separately.

CHAPTER III

BRACKETING FUNCTION AND FIRST ORDER ITERATION OF EIGENVALUES

Using some of the equations derived in Chapter II, we will now introduce a function $f(\mathcal{E})$ called bracketing function. Only the eigenvalues of $\mathcal{H}^m$ different from those of $\mathcal{H}^n$ are bracketed consecutively by use of first order iteration.

From (2.20), for each root E of $\overline{Y}(\mathcal{E})$, one obtains

$$\mathcal{H}_{mm} - E = \frac{\sum_{k=1}^{n} V_{mk}^2 \left[\prod_{\substack{i=1 \\ (i\neq k)}}^{n} (h_i - E) \right]}{\prod_{i=1}^{n} (h_i - E)} \tag{3.1a}$$

for the case that all roots h_i are distinct and all V_{mk} are non-vanishing. In case there are degeneracies in the spectrum of $\mathcal{H}^n$ one obtains for the roots of $\overline{Y}(\mathcal{E})$ as defined in (2.31):

$$\mathcal{H}_{mm} - E = \frac{\sum_{k=1}^{\ell} W_{mk}^2 \left[\prod_{\substack{i=1 \\ (i\neq k)}}^{\ell} (h_i - E) \right]}{\prod_{i=1}^{\ell} (h_i - E)} \tag{3.1b}$$

and for the case V_{mj} vanishes, one has, from (2.35)

$$\mathcal{H}_{mm} - E = \frac{\sum_{\substack{k=1 \\ (k\neq j)}}^{n} V_{mk}^2 \left[\prod_{\substack{i\neq k \\ (i\neq k, i\neq j)}}^{n} (h_i - E) \right]}{\prod_{\substack{i=1 \\ (i\neq j)}}^{n} (h_i - E)} \tag{3.1c}$$

We note here that (3.1b) does not indicate the degree of degeneracy of h_i and (3.1c) is independent of h_j(the corresponding V_{mj}^2 is vanishing). In the later applications of (3.1b) and (3.1c) to the iteration process, where ϕ_m is the reference function of a one-dimensional manifold one has to note that there is no information about the degree of degeneracy nor about the eigenvalue h_j corresponding to a vanishing V_{mj}.

In this sense, the eigenvalue of h_j is lost[8]. With these facts in mind, we will primarily work with (3.1a). One can write (3.1a) in the form

$$E = f(E) \tag{3.2}$$

for an eigenvalue E, where the function f is defined by

$$f(\mathcal{E}) \equiv H_{mm} - \sum_{k=1}^{n} \frac{V_{mk}^2}{(h_k - \mathcal{E})} \tag{3.3}$$

for the continuous variable $\mathcal{E}$. Since $f'(\mathcal{E}) < 0$:

$$\frac{\partial f(\mathcal{E})}{\partial \mathcal{E}} = - \sum_{k=1}^{n} \frac{V_{mk}^2}{(h_k - \mathcal{E})^2} < 0 \ , \tag{3.4}$$

$\mathcal{E}$ and $f(\mathcal{E})$ will bracket at least one eigenvalue E[8]. In this sense, we will call $f(\mathcal{E})$ a "bracketing function."

It is interesting to derive the bracketing function by use of the partitioning process and we will introduce Löwdin's[8,12] development of the partitioning technique in terms of an operator formalism. Let $\mathcal{O}$ be a self-adjoint projection operator which defines a certain subspace $S(\mathcal{O})$ of order g in the total Hilbert space, so that

$$\mathcal{O}^2 = \mathcal{O}; \qquad \mathcal{O}^+ = \mathcal{O}; \qquad \mathrm{Tr}(\mathcal{O}) = g \quad [*3] \quad . \tag{3.5}$$

The orthogonal complement to the subspace $S(\mathcal{O})$ is defined by the operator $P = 1 - \mathcal{O}$, which satisfies the relations

$$P^2 = P, \qquad P^+ = P \quad \text{and} \quad \mathcal{O}P = P\mathcal{O} = 0. \tag{3.6}$$

Let us further introduce the operator $T = T(\mathcal{E})$ by the definition

$$T(\mathcal{E}) = P[\alpha \cdot \mathcal{O} + P(\mathcal{E} - \mathcal{H})P]^{-1}P \quad , \tag{3.7}$$

where $\alpha \neq 0$ is an arbitrary number. In the following we will often use the symbolic notation

$$T = \frac{P}{(\mathcal{E} - \mathcal{H})} \quad . \tag{3.8}$$

It is seen that T fulfills the following relations:

$$P(\mathcal{E} - \mathcal{H})T = P \quad , \tag{3.9}$$

$$\mathcal{O}T = T\mathcal{O} = 0 \quad . \tag{3.10}$$

Let us now consider the operator Ω defined by the relation

$$\Omega(\mathcal{E}) = \mathcal{O} + T(\mathcal{E})\mathcal{H}\mathcal{O} \, . \tag{3.11}$$

Using (3.9), we obtain the identity

$$P(\mathcal{H} - \mathcal{E})\Omega = P(\mathcal{H} - \mathcal{E})\mathcal{O} + P(\mathcal{H} - \mathcal{E})T\mathcal{H}\mathcal{O} = P\mathcal{H}\mathcal{O} - P\mathcal{H}\mathcal{O} = 0 \, . \tag{3.12}$$

[*3] In practical applications of the partitioning technique, we often utilize the bracketing property of the first order iteration procedure. In these problems the choice of an arbitrary subspace $S(\mathcal{O})$ has some importance in connection with the convergence property of the iteration method. In this sense for $g = 1$, we will call the subspace $S(\mathcal{O})$ a one-dimensional reference manifold, and for $g \geq 2$, we will call it a multi-dimensional reference manifold.

for all values of $\mathcal{E}$. Hence we have

$$(\mathcal{H}-\mathcal{E})\Omega = (\mathcal{O}+\mathrm{P})(\mathcal{H}-\mathcal{E})\Omega = \mathcal{O}(\mathcal{H}-\mathcal{E})\Omega$$

$$= \mathcal{O}(\mathcal{H}-\mathcal{E})(\mathcal{O}+\mathrm{T}\mathcal{H}\mathcal{O})$$

$$= \mathcal{O}(\mathcal{H}+\mathcal{H}\mathrm{T}\mathcal{H}-\mathcal{E})\mathcal{O} \quad .$$

If $\Omega(\mathrm{E})\phi$ is an eigenfunction of $\mathcal{H}$ with an eigenvalue E, ϕ has to satisfy the relation

$$(\mathcal{H}-\mathrm{E})\Omega(\mathrm{E})\phi = 0 \quad , \tag{3.13}$$

or

$$\mathrm{E}\,\mathcal{O}\phi = \mathcal{O}(\mathcal{H}+\mathcal{H}\mathrm{T}_{(\mathrm{E})}\mathcal{H})\mathcal{O}\phi \quad . \tag{3.14}$$

This is the necessary and sufficient condition for E to be an eigenvalue of $\mathcal{H}$. Let

$$\mathcal{O} = \sum_{i=1}^{g} |\phi_i\rangle\langle\phi_i| \quad , \tag{3.15}$$

with

$$\langle\phi_i|\phi_j\rangle = \delta_{ij} \quad .$$

Then the condition (3.14) gives

$$\sum_{j=1}^{g} (\bar{\mathcal{H}}_{ij} - \mathrm{E}\delta_{ij})\langle\phi_j|\phi\rangle = 0 \quad , \qquad (i=1,2,\ldots,g) \tag{3.16}$$

where

$$\bar{\mathcal{H}}_{(\mathrm{E})} = \mathcal{H} + \mathcal{H}\mathrm{T}_{(\mathrm{E})}\mathcal{H} \quad , \tag{3.17}$$

$$\bar{\mathcal{H}}_{ij} = \langle\phi_i|\bar{\mathcal{H}}|\phi_j\rangle \quad .$$

From (3.16), we see that E has to satisfy the secular equation

$$\begin{vmatrix} \bar{\mathcal{H}}_{11}-E & \bar{\mathcal{H}}_{12} & \cdots & \bar{\mathcal{H}}_{1g} \\ \bar{\mathcal{H}}_{21} & \bar{\mathcal{H}}_{22}-E & \cdots & \bar{\mathcal{H}}_{2g} \\ \cdot & \cdot & \cdots & \cdot \\ \bar{\mathcal{H}}_{g1} & \bar{\mathcal{H}}_{g2} & \cdots & \bar{\mathcal{H}}_{gg}-E \end{vmatrix} = 0, \qquad (3.18)$$

and further $\mathcal{O}\phi$ cannot be arbitrary if $\mathrm{Tr}(\mathcal{O}) = g > 1$, because the components $\langle \phi_j | \phi \rangle$ must be eigenvectors of $\bar{\mathcal{H}}(E)$. We will work with (3.18) in more detail in Chapter V in connection with the multi-dimensional manifold.

Let us now define an operator $\mathcal{H}'$:

$$\mathcal{H}' = P\mathcal{H}P \quad , \qquad (3.19)$$

and its eigenfunctions Ψ_i', so that

$$\mathcal{H}'\Psi_i' = h_i\Psi_i' \qquad (i=1,2,\ldots,) \qquad (3.20)$$

then

$$T(E) = \sum_{i=1}^{\infty} \frac{|\Psi_i'\rangle\langle\Psi_i'|}{(E - h_i)} \qquad (3.21)$$

$$\bar{\mathcal{H}}(E) = \mathcal{H} + \sum_{i=1}^{\infty} \frac{\mathcal{H}|\Psi_i'\rangle\langle\Psi_i'|\mathcal{H}}{(E - h_i)} \qquad (3.22)$$

For the case g = 1, one can put $\mathcal{O} = |\varphi\rangle\langle\varphi|$, with $\langle\varphi|\varphi\rangle = 1$, then (3.16) reads simply

$$(\bar{\mathcal{H}}_{11} - E)\langle\varphi|\phi\rangle = 0. \qquad (3.23)$$

Assuming $\langle \varphi | \phi \rangle \neq 0$, one obtains

$$E = \langle \varphi | \mathcal{H} | \varphi \rangle$$

$$= \langle \varphi | \mathcal{H} + \mathcal{H} T_{(E)} \mathcal{H} | \varphi \rangle \qquad (3.24)$$

$$= \langle \varphi | \mathcal{H} | \varphi \rangle + \langle \varphi | \mathcal{H} T_{(E)} \mathcal{H} | \varphi \rangle$$

The introduction of (3.21) into (3.24) gives

$$E = \langle \varphi | \mathcal{H} | \varphi \rangle + \sum_{i=1}^{\infty} \frac{\langle \varphi | \mathcal{H} | \Psi_i \rangle \langle \Psi_i | \mathcal{H} | \varphi \rangle}{(E - h_i)} \qquad (3.25)$$

If we put

$$\mathcal{H}_{mm} \equiv \langle \varphi | \mathcal{H} | \varphi \rangle \ ,$$

and

$$V_{mi} = \langle \varphi | \mathcal{H} | \Psi_i' \rangle \ ,$$

then it is seen that (3.24) is of the same form as (3.3), which indicates that the function $f(\mathcal{E})$ defined by

$$f(\mathcal{E}) \equiv \langle \varphi | \mathcal{H} | \varphi \rangle + \langle \varphi | \mathcal{H} T_{(\mathcal{E})} \mathcal{H} | \varphi \rangle \qquad (3.26)$$

is a bracketing function of E.

The first order iteration, using this bracketing property, will be convergent if $\left| \frac{\partial f(\mathcal{E})}{\partial \mathcal{E}} \right| < 1$, and will be divergent if $\left| \frac{\partial f(\mathcal{E})}{\partial \mathcal{E}} \right| > 1$ [12]. In this connection, the choice of the reference function is important.

In the treatment of a Hamiltonian $\mathcal{H}$ which can be written as the sum of two terms, $\mathcal{H} = \mathcal{H}^{\circ} + V$, it is convenient to introduce a reduced resolvent T_o and a reaction operator t through the relations:

$$T_{o(\mathcal{E})} = \frac{P}{(\mathcal{E} - \mathcal{H}^{\circ})} \qquad (3.27)$$

$$t(\mathcal{E}) = V + V T_{(\mathcal{E})} V \qquad (3.28)$$

However, practically, it is often difficult to work directly with the reaction operator $t(\mathcal{E})$, and we are obliged to develop some method which gives an operator $t'(\mathcal{E})$ characterized by the inequality

$$t'(\mathcal{E}_o) < t(\mathcal{E}_o) \quad [*4] \tag{3.33}$$

Then (3.32a) and (3.32b) are replaced by

$$\mathcal{E}_1' \equiv \langle \bar{\varphi} | \mathcal{H}^o | \varphi^o \rangle + \langle \bar{\varphi} | t'(\mathcal{E}_o) | \bar{\varphi} \rangle, \tag{3.34}$$

$$\mathcal{E}_1' \equiv \langle \varphi^o | \mathcal{H}^o | \varphi^o \rangle + \langle \varphi^o | t'(\mathcal{E}_o) | \varphi^o \rangle, \tag{3.35}$$

and we have the following inequalities:

$$\mathcal{E}_1' < \mathcal{E}_1 < E < \mathcal{E}_o \tag{3.36}$$

A useful way to achieve this end is to introduce the concept of the "inner projection"[6] as discussed in the next chapter.

[*4] $A \leq B$ means $\langle \Psi | A | \Psi \rangle \leq \langle \Psi | B | \Psi \rangle$ for every Ψ in the common domain of A and B.

The operators T_o and t will hence depend on $\mathcal{E}$. Using (3.26) we will try to find a practical method for obtaining lower bounds.

By using the relations $TV = T_o t$ and $T = T_o + T_o t T_o$, Löwdin has derived[7] the following transformation for the operator $\mathcal{H}$

$$\bar{\mathcal{H}} = \mathcal{H} + \mathcal{H}T\mathcal{H} = (\mathcal{H}^o + \mathcal{H}^o T_o \mathcal{H}^o) + (1 + \mathcal{H}^o T_o) t (1 + T_o \mathcal{H}^o). \quad (3.29)$$

Substitution of this expression into (3.26) gives

$$\begin{aligned} f(\mathcal{E}) &= \langle \varphi | \mathcal{H}^o | \bar{\varphi} \rangle + \langle \bar{\varphi} | t | \bar{\varphi} \rangle \\ &= \langle \bar{\varphi} | \mathcal{H}^o | \varphi \rangle + \langle \bar{\varphi} | t | \bar{\varphi} \rangle \end{aligned} \quad (3.30)$$

where $$\bar{\varphi} = (1 + T_o \mathcal{H}^o)\varphi$$

In connection with the solvability of the Schrödinger equation $\mathcal{H}^o \varphi^o = E^o \varphi^o$, it is convenient to take φ^o as a reference function, since for this case (3.30) simply reads

$$\begin{aligned} f(\mathcal{E}) &= E^o + \langle \varphi^o | V + V T(\mathcal{E}) V | \varphi^o \rangle \\ &= E^o + \langle \varphi^o | t(\mathcal{E}) | \varphi^o \rangle \end{aligned} \quad (3.31)$$

In principle we can obtain the upper bound $\mathcal{E}_o$ to any desired accuracy and by use of the bracketing property, (3.30) or (3.31), we can estimate a lower bound $\mathcal{E}_1$:

$$\mathcal{E}_1 = f(\mathcal{E}_o) = \langle \bar{\varphi} | \mathcal{H}^o | \varphi \rangle + \langle \bar{\varphi} | t(\mathcal{E}_o) | \bar{\varphi} \rangle , \quad (3.32a)$$

$$\mathcal{E}_1 = f(\mathcal{E}_o) = \langle \varphi^o | \mathcal{H}^o | \varphi^o \rangle + \langle \varphi^o | t(\mathcal{E}_o) | \varphi^o \rangle . \quad (3.32b)$$

CHAPTER IV

THE ONE-DIMENSIONAL REFERENCE MANIFOLD AND LOWER BOUNDS

Löwdin[6,7] has developed a method for the estimation of lower bounds to the energy eigenvalues of the Hamiltonian $\mathcal{H} = \mathcal{H}^0 + V$. In this method, in order to avoid the ordering theorem of the "Intermediate Hamiltonian"[13,14], the bracketing theorem as well as the concept of "inner projection" is used.

Let A be a positive definite, self-adjoint operator. Denoting the eigenvalues and eigenfunctions of A by a_i and U_i, respectively, one obtains the spectral resolution

$$A = \sum_i a_i |U_i\rangle\langle U_i| \quad , \tag{4.1}$$

with $a_i > 0$.

Let us further define an operator $A^{\frac{1}{2}}$ by the relation

$$A^{\frac{1}{2}} = \sum_i a_i^{\frac{1}{2}} |U_i\rangle\langle U_i| \; ; \tag{4.2}$$

then the "inner projection" of A, A', is defined by

$$A' = A^{\frac{1}{2}} Q^n A^{\frac{1}{2}} \quad , \tag{4.3}$$

where Q^n is a Hermitian projection operator on a linear manifold F_n, which is spanned by a set of linearly independent functions,

$$\mathfrak{f} \equiv (f_1, f_2, \ldots, f_n). \tag{4.4}$$

Denoting the adjoint of $\mathfrak{f}$ by

$$\mathfrak{f}^{+} \equiv \begin{pmatrix} f_1^{*} \\ f_2^{*} \\ \cdot \\ \cdot \\ \cdot \\ f_n^{*} \end{pmatrix} , \tag{4.5}$$

one obtains the corresponding metric matrix

$$\Delta \equiv \mathfrak{f}^{+}\mathfrak{f} \equiv \langle \mathfrak{f} | \mathfrak{f} \rangle . \tag{4.6}$$

A typical element of Δ is defined by

$$\Delta_{kl} = \langle f_k | f_l \rangle . \tag{4.7}$$

With this notation one can define a Hermitian projection operator Q^n by

$$Q^n = \mathfrak{f} \Delta^{-1} \mathfrak{f}^{+} \equiv |\mathfrak{f}\rangle \Delta^{-1} \langle \mathfrak{f}| , \tag{4.8}$$

with the property

$$Q^n Q^n = Q^n, \quad Q^{n\dagger} = Q^n \text{ and } \mathrm{Tr}(Q^n) = n . \tag{4.9}$$

Then (4.3) will have the form

$$A' = A^{\frac{1}{2}} |\mathfrak{f}\rangle \Delta^{-1} \langle \mathfrak{f}| A^{\frac{1}{2}} . \tag{4.10}$$

If we incorporate one more function, say f_{n+1}, into the set $\mathfrak{f}$ and denote the corresponding projection operator by Q^{n+1} with the property

$$Q^{n+1} Q^{n+1} = Q^{n+1}, \quad Q^{n+1^{+}} = Q^{n+1} \text{ and } \mathrm{Tr}(Q^{n+1}) = n+1, \tag{4.11}$$

then one obtains[9]

$$Q^{n+1}Q^n = Q^nQ^{n+1} = Q^n \tag{4.12}$$

Equations (4.9), (4.10) and (4.11), together with the relations

$$\begin{aligned} Q^n &= Q^nQ^n = Q^{n^+}Q^n \geq 0 \quad , \\ (1-Q^{n+1})^+(1-Q^{n+1}) &\geq 0 \quad , \\ (Q^{n+1}-Q^n)^+(Q^{n+1}-Q^n) &\geq 0 \end{aligned} \tag{4.13}$$

give the inequality

$$0 \leq Q^n \leq Q^{n+1} \leq 1 \tag{4.14}$$

or

$$0 \leq A^{\frac{1}{2}}Q^nA^{\frac{1}{2}} \leq A^{\frac{1}{2}}Q^{n+1}A^{\frac{1}{2}} \leq A \quad . \tag{4.15}$$

Thus, by enlarging the space F_n, the "inner projection" A' approaches A.

In the following it is convenient to introduce three more manifolds $\mathcal{g} \equiv (g_1,g_2,\ldots,g_n)$, $\mathcal{h} \equiv (h_1,h_2,\ldots,h_n)$ and $\mathcal{j} \equiv (j_1,j_2,\ldots,j_n)$ defined by the relations

$$\mathcal{f} = A^{\frac{1}{2}}\mathcal{g} \quad , \quad \mathcal{f} = A^{-\frac{1}{2}}\mathcal{h} \quad \text{and} \quad \mathcal{f} = A^{-\frac{1}{2}}(\varepsilon - \mathcal{H}^o)\,\mathcal{j} \quad . \tag{4.16}$$

Substitution of (4.16) into (4.3) gives

$$A' = A|\mathcal{g}\rangle\Delta^{-1}\langle\mathcal{g}|A \tag{4.17}$$

with

$$\Delta = \langle\mathcal{g}|A|\mathcal{g}\rangle \tag{4.18}$$

$$A' = |\mathcal{h}\rangle\Delta^{-1}\langle\mathcal{h}| \tag{4.19}$$

with

$$\Delta = \langle\mathcal{h}|A^{-1}|\mathcal{h}\rangle \tag{4.20}$$

and $$A' = (\mathcal{E}-\mathcal{H}^{\circ})|\mathring{\mathcal{J}}\rangle \Delta^{-1} \langle \mathring{\mathcal{J}}|(\mathcal{E}-\mathcal{H}^{\circ}) \tag{4.21}$$

with $$\Delta = \langle \mathring{\mathcal{J}}|(\mathcal{E}-\mathcal{H}^{\circ}) A^{-1} (\mathcal{E}-\mathcal{H}^{\circ})|\mathring{\mathcal{J}}\rangle \tag{4.22}$$

The "inner projection" in the form of (4.10) is called by Löwdin[7] the "standard inner projection" whereas (4.17) and (4.19) are called the "Aronszajn projection" and the "Bazley projection," respectively. Since the "inner projection" of the form (4.21) was first introduced by Löwdin[6,15], we may call it the "Löwdin projection." For convenience we will also call the manifolds $\mathcal{F}$, $\mathcal{G}$, $\mathcal{H}$ and $\mathring{\mathcal{J}}$ the "standard space," the "Aronszajn space," the "Bazley space" and the "Löwdin space," respectively[7].

According to (3.32a), the two quantities $\mathcal{E}_o$ and $\mathcal{E}_1$, which bracket a true eigenvalue E are connected by the relation

$$\mathcal{E}_1 = \langle \bar{\Phi}|\mathcal{H}^{\circ}|\Phi\rangle + \langle \bar{\Phi}|\mathcal{T}(\mathcal{E}_o)|\bar{\Phi}\rangle,$$

where $\mathcal{E}_o$ is an upper bound to E and $\mathcal{E}_1$ is a lower bound to E. Furthermore if one can evaluate $\mathcal{E}_1'$ which is smaller than $\mathcal{E}_1$:

$$\mathcal{E}_1' \leq \mathcal{E}_1 < E < \mathcal{E}_o \quad , \tag{4.23}$$

then $\mathcal{E}_1'$ is a lower bound to E. This can be accomplished by introducing the operator t' which is smaller than t. If t is positive definite we can always obtain t' by means of an "inner projection,"

$$t' = t^{\frac{1}{2}} Q^n t^{\frac{1}{2}} \quad . \tag{4.24}$$

Löwdin[7] has shown that, even if t is not positive definite, we can form t' such that $t' \leq t$ for a positive definite perturbation V.

Consider an energy level of $\mathcal{H}$ whose upper bound $\mathcal{E}_o$ satisfies the inequality

$$\mathcal{E}_o < E^o_{p+1} \quad , \tag{4.25}$$

where E^o_{p+1} is the $(p+1)^{th}$ eigenvalue of $\mathcal{H}^o$ from below. Then the choice of an Aronszajn space for the inner projection of V so that

$$V' = V|\mathcal{G}\rangle\langle\mathcal{G}|V|\mathcal{G}\rangle^{-1}\langle\mathcal{G}|V \, ,$$

is sufficient to satisfy the inequality $t'(\mathcal{E}_o) \leq t(\mathcal{E}_o)$,

where $$t' = V' + V'TV' \tag{4.26}$$

$$= V|\mathcal{G}\rangle\langle\mathcal{G}|V - VT_o V|\mathcal{G}\rangle^{-1}\langle\mathcal{G}|V \, ,$$

if $\mathcal{G}$ includes all the lower lying unperturbed eigenfunctions Ψ^o_i with respect to E^o_{p+1}. Hence the minimum requirement for $\mathcal{G}$ is given by

$$\mathcal{G} = \{ \Psi^o_1, \Psi^o_2, \ldots \Psi^o_p \} \, . \tag{4.27}$$

This choice of the manifold is conveniently applied to the problems where $V\mathcal{G}$ can be expressed in terms of a known finite number of eigenfunctions of $\mathcal{H}^o$[16].

One example of this case will be given in Chapter VI.

Bazley and Fox[17,18] have discussed the similar cases in connection with their special choice of linear manifold.

CHAPTER V

THE MULTI-DIMENSIONAL REFERENCE MANIFOLD AND LOWER BOUNDS

The main difficulty in the use of (3.34) or (3.35) for the calculation of lower bounds is that, for an upper bound $\mathcal{E}_o$ greater than the first excited state E_2^o of $\mathcal{H}^o$, the generalized reaction opertor $t(\mathcal{E}_o)$ is not positive definite. Even though we can circumvent this difficulty by use of (4.26), its applicability is rather limited due to the appearance of the reduced resolvent T_o in t. These two difficulties and the ordering theorem are avoided by use of the multi-dimensional reference space in the partitioning technique. The general outline of this partitioning process is introduced in Chapter III.

Let us consider the operator $\bar{\mathcal{H}}$ and $\tilde{\mathcal{H}}$ defined by

$$\bar{\mathcal{H}}_{(\mathcal{E})} \equiv \mathcal{H} + \mathcal{H} T_{(\mathcal{E})} \mathcal{H}, \tag{5.1}$$

and

$$\tilde{\mathcal{H}}_{(\mathcal{E})} \equiv \mathcal{O} \bar{\mathcal{H}}_{(\mathcal{E})} \mathcal{O}, \tag{5.2}$$

where $\mathcal{O}$ is a Hermitian projection operator defined in (3.5) with Tr $(\mathcal{O})$ = g. Since $T(\mathcal{E})$ is a function of $\mathcal{E}$, so is $\bar{\mathcal{H}}$ and $\tilde{\mathcal{H}}$, and g eigenvalues of $\tilde{\mathcal{H}}(\mathcal{E})$ will change continuously with $\mathcal{E}$ except at some singular points. At this point, it is convenient to consider an eigenvalue

problem of the form

$$\tilde{\mathcal{H}}_{(\mathcal{E})}\phi_i = \epsilon_i\phi_i \quad , \qquad (i=1,2,\ldots,g). \qquad (5.3)$$

It is seen that (3.14) is a particular case of (5.3) with both $\mathcal{E}$ and ϵ_i equal to E which is an eigenvalue of $\mathcal{H}$.

Using the property of the complementary projection operator P:

$$P = 1 - \mathcal{O}$$

we see that

$$P\tilde{\mathcal{H}}_{(\mathcal{E})} = 0$$

and any function in S(P) *5 is an eigenvector with an eigenvalue zero for all values of $\mathcal{E}$; this case is of little interest in connection with the partitioning technique, and we will confine ourselves to $S(\mathcal{O})$ so that

$$P\phi_i = 0. \qquad (5.4)$$

Therefore for eigenfunctions of $\mathcal{H}$ which are in S(P), this partitioning process fails to give the corresponding eigenvalues.

Theorem 5.1. If $\mathcal{E}$ is equal to one of the eigenvalues of $\tilde{\mathcal{H}}_{(\mathcal{E})}$, ϵ_i, i.e., $\epsilon_i(\mathcal{E}) = \mathcal{E}$, then ϵ_i is an eigenvalue of $\mathcal{H}$.

Proof: Starting from (5.3), one obtains

$$\tilde{\mathcal{H}}_{(\epsilon_i)}\phi_i = \epsilon_i\phi_i \quad , \qquad (5.5)$$

---

*5 It is convenient to refer to the subspace associated with the P as S(P).

$$Q(\mathcal{H} + \mathcal{H} T(\epsilon_i) \mathcal{H}) Q \phi_i = \epsilon_i Q \phi_i ,$$

$$Q \mathcal{H} (Q + T(\epsilon_i) \mathcal{H} Q) \phi_i = \epsilon_i Q (1 + T(\epsilon_i) \mathcal{H} Q) \phi_i ,$$

$$Q (\mathcal{H} - \epsilon_i)(Q + T(\epsilon_i) \mathcal{H} Q) = 0. \qquad (5.6)$$

Since

$$P (\mathcal{H} - \epsilon_i)(Q + T(\epsilon_i) \mathcal{H} Q) = 0, \qquad \text{by (3.12)},$$

$$(Q + P)(\mathcal{H} - \epsilon_i)(Q + T(\epsilon_i) \mathcal{H} Q) \phi_i = 0,$$

or $$(\mathcal{H} - \epsilon_i)(Q + T(\epsilon_i) \mathcal{H} Q) \phi_i = 0 ; \qquad (5.7)$$

this indicates that $(Q + T(\epsilon_i) \mathcal{H} Q) \phi_i$ is an eigenfunction of $\mathcal{H}$ with an eigenvalue ϵ_i. Q.E.D.

Furthermore from the relations (3.17) and (3.18) there follows:

Corollary 5.1. If E is an eigenvalue of $\mathcal{H}$, but not an eigenvalue of $P \mathcal{H} P$, then E is also an eigenvalue of $\tilde{\mathcal{H}}(E)$.

In Figure 1, the relation between the eigenvalues of $\tilde{\mathcal{H}}(\mathcal{E})$ and those of $\mathcal{H}$ are schematically illustrated and in order to explain this figure we will discuss the asymptotic behavior of the eigenvalues of $\tilde{\mathcal{H}}(\mathcal{E})$ as $\mathcal{E}$ varies from $-\infty$ to ∞. From (3.22) one obtains for $\tilde{\mathcal{H}}(\mathcal{E})$.

$$\begin{aligned} \tilde{\mathcal{H}}(\mathcal{E}) &= Q \bar{\mathcal{H}} Q \\ &= Q (\mathcal{H} + \mathcal{H} T_{(\mathcal{E})} \mathcal{H}) Q \\ &= Q \left(\mathcal{H} + \sum_{i=1}^{\infty} \frac{\mathcal{H} |\Psi_i'\rangle \langle \Psi_i'| \mathcal{H}}{(\mathcal{E} - h_i)} \right) Q , \end{aligned} \qquad (5.8)$$

where $\mathcal{H}' = P \mathcal{H} P$ and $\mathcal{H}' \Psi_i' = h_i \Psi_i'$.

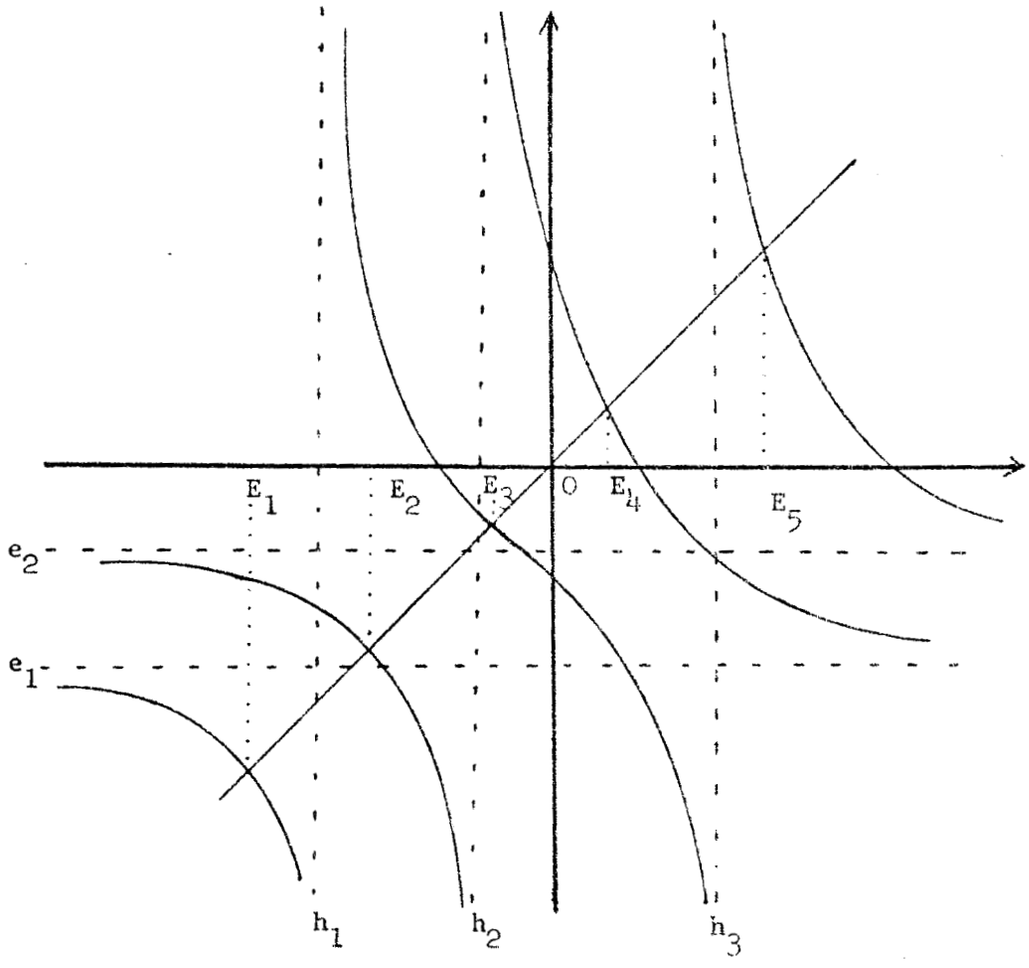

Fig. 1. The graphical construction of the eigenvalues of $\mathbb{H}$.

E_1, E_2, E_3, E_4 and E_5 denote the eigenvalues of $\mathbb{H}$; and h_1, h_2, and h_3 denote the eigenvalues of $\mathbb{H}_{bb}$; and e_1 and e_2 denote the eigenvalues of $\mathbb{H}_{aa}$. The author is indebted to Professor P. O. Löwdin for showing this diagram.

It is sometimes more convenient to consider this partitioning process in terms of a secular equation of a finite dimension and later extend this to the infinite Hilbert space to match with the operator formalism shown above.

If one uses an orthonormal basis $\{\phi\}_g = \{\phi_1, \phi_2, \ldots, \phi_g\}$ in expressions (2.5) and (2.6), one obtains the matrix equation

$$\mathbb{H}\,\mathbb{C} = E\,\mathbb{C} \tag{5.9}$$

with $$\mathcal{H}_{k\ell} = \langle \phi_k | \mathcal{H} | \phi_\ell \rangle \ , \tag{5.10}$$

and $$\langle \phi_k | \phi_\ell \rangle = \delta_{k\ell} \ . \tag{5.11}$$

Let us now "partition" the basis into two subsets (a) and (b) and denote the associated subspaces by S(a) and S(b), respectively. The matrix $\mathbb{H}$ and the vector $\mathbb{C}$ may be written in the form

$$\mathbb{H} = \begin{pmatrix} \mathbb{H}_{aa} & \mathbb{H}_{ab} \\ \mathbb{H}_{ba} & \mathbb{H}_{bb} \end{pmatrix} \ , \qquad \mathbb{C} = \begin{pmatrix} \mathbb{C}_a \\ \mathbb{C}_b \end{pmatrix} \ ; \tag{5.12}$$

and instead of (5.9), two equations result:

$$\mathbb{H}_{aa}\mathbb{C}_a + \mathbb{H}_{ab}\mathbb{C}_b = E\,\mathbb{C}_a \ , \tag{5.13}$$

$$\mathbb{H}_{ba}\mathbb{C}_a + \mathbb{H}_{bb}\mathbb{C}_b = E\,\mathbb{C}_b \ . \tag{5.14}$$

If the eigenvalue E of $\mathbb{H}$ is different from the eigenvalues of $\mathbb{H}_{bb}$, (5.14) gives

$$\mathbb{C}_b = (E\,\mathbb{I}_{bb} - \mathbb{H}_{bb})^{-1}\,\mathbb{H}_{ba}\,\mathbb{C}_a \ . \tag{5.15}$$

Substitution of (5.15) into (5.13) leads to the relation

$$\overline{\mathcal{H}}_{aa}\, C_a = E\, C_a, \tag{5.16}$$

where

$$\overline{\mathcal{H}}_{aa} = \mathcal{H}_{aa} + \mathcal{H}_{ab}\,(E\,\mathbb{1}_{bb} - \mathcal{H}_{bb})^{-1}\,\mathcal{H}_{ba}. \tag{5.17}$$

If the inverse of $(E\,\mathbb{1}_{bb} - \mathcal{H}_{bb})$ exists, (5.15) gives the relation between C_a and C_b and if (5.16) can be solved, C_b can be obtained by (5.15). However for an eigenvalue of $\mathcal{H}$ which is equal to one of the eigenvalues of $\mathcal{H}_{bb}$, this partitioning device fails to give the eigenfunctions as well as the eigenvalues, and in this sense the eigenvalue is lost (see the statement after (5.4)).

Equation (5.16) has exactly the same form as (5.3), with the understanding that S(b) is extended to the Hilbert space of infinite order orthogonal to S(a). Transforming the matrix $\mathcal{H}$ by means of the unitary transformation

$$\left(\begin{array}{c|c} \mathbb{1}_{aa} & 0 \\ \hline 0 & U_{bb} \end{array}\right), \tag{5.18}$$

where the matrix U_{bb} is composed of the eigenvectors of $\mathcal{H}_{bb}$, one obtains the equivalent matrix $\mathcal{H}'$ of the form shown in (5.19)

$$\mathcal{H}' \equiv \left(\begin{array}{c|c} \mathcal{H}_{aa} & \mathcal{H}_{ab}U_{bb} \\ \hline U_{bb}^{+}\mathcal{H}_{ba} & U_{bb}^{+}\mathcal{H}_{bb}U_{bb} \end{array}\right) \equiv \left(\begin{array}{c|c} \mathcal{H}_{aa} & \mathcal{H}'_{ab} \\ \hline \mathcal{H}'_{ba} & \mathcal{H}'_{bb} \end{array}\right) \tag{5.19}$$

or

$$H' = \begin{pmatrix} H_{aa} & H'_{ab} \\ \hline H'_{ba} & \begin{matrix} h_1 & 0 & \cdots \\ 0 & h_2 & \\ \vdots & & \ddots \end{matrix} \end{pmatrix} \qquad *6 \qquad (5.20)$$

where h_1, h_2, ..., are eigenvalues of H_{bb}. From this matrix H' one obtains the equivalent form of (5.17)

$$\overline{H}_{aa} = H_{aa} + H'_{ab}(E\,\mathbb{1}_{bb} - H'_{bb})^{-1} H'_{ba}, \qquad (5.21)$$

where the matrix $(E\,\mathbb{1}_{bb} - H'_{bb})^{-1}$ has the diagonal form with an element $\frac{1}{(E - h_i)}$ for the i^{th} element. Equation (5.21) is equivalent to (5.8).

It is seen from (5.8) and (5.21) that there are two types of asymptotes for the eigenvalues of $\tilde{\mathcal{H}}(\mathcal{E})$ (or $\overline{H}_{aa}(\mathcal{E})$) corresponding to the eigenvalues of $\mathcal{O}\mathcal{H}\mathcal{O}$ (or H_{aa}) and $\mathcal{P}\mathcal{H}\mathcal{P}$ (or H_{bb}), the former is horizontal and the latter is vertical. The number of asymptotes of each type is given by the number of distinct eigenvalues of $\mathcal{O}\mathcal{H}\mathcal{O}$ and $\mathcal{P}\mathcal{H}\mathcal{P}$, respectively. However the common eigenvalues, if they exist, of $\mathcal{H}$ and $\mathcal{P}\mathcal{H}\mathcal{P}$ are eliminated here.

In order to examine the behavior of the eigenvalues of $\tilde{\mathcal{H}}(\mathcal{E})$ (or $\overline{H}_{aa}(\mathcal{E})$) qualitatively, an example is considered where the dimension of S(a) is two and the dimension of S(b) is three. The operator formalism and the matrix formalism will be used interchangeably according to convenience. Consider the non-degenerate case of H_{aa}

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*6 We assume here that the unitary transformation(5.18) is so arranged that $h_1 \leq h_2 \leq h_3 \ldots$.

and denote the eigenvalues of $\mathbb{H}_{aa}$ by e_1 and e_2 (with $e_1 < e_2$) and those of $\mathbb{H}_{bb}$ by h_1, h_2 and h_3, respectively.

Assuming S(a) is spanned by ϕ_1 and ϕ_2 and S(b) is spanned by ϕ_3, ϕ_4 and ϕ_5, (5.21) has the form

$$\overline{\mathbb{H}}_{aa}(\varepsilon) = \mathbb{H}_{aa} + \mathbb{H}'_{ab}(\varepsilon \mathbb{I}_{bb} - \mathbb{H}'_{bb})^{-1} \mathbb{H}'_{ba} \qquad (5.22)$$

with

$$\mathbb{H}_{aa} = \begin{pmatrix} \mathcal{H}_{11} & \mathcal{H}_{12} \\ \mathcal{H}_{21} & \mathcal{H}_{22} \end{pmatrix}$$

and

$$\mathbb{H}'_{ab}(\varepsilon \mathbb{I}_{bb} - \mathbb{H}'_{bb})^{-1}\mathbb{H}'_{ba} = \sum_{i=3}^{5} \begin{pmatrix} \frac{\mathcal{H}'_{1i}\mathcal{H}'_{i1}}{\varepsilon - \mathcal{H}'_{ii}} & \frac{\mathcal{H}'_{1i}\mathcal{H}'_{i2}}{\varepsilon - \mathcal{H}'_{ii}} \\ \frac{\mathcal{H}'_{2i}\mathcal{H}'_{i1}}{\varepsilon - \mathcal{H}'_{ii}} & \frac{\mathcal{H}'_{2i}\mathcal{H}'_{i2}}{\varepsilon - \mathcal{H}'_{ii}} \end{pmatrix}. \qquad (5.23)$$

Note that h_1 in Fig. 1 is related to $\mathcal{H}'_{jj}$ by

$$h_1 = \mathcal{H}'_{33},\ h_2 = \mathcal{H}'_{44},\ \text{and}\ h_3 = \mathcal{H}'_{55}\ . \qquad (5.24)$$

Defining

$$\mathbb{H}'_{aa}(\varepsilon) \equiv \mathbb{H}'_{ab}(\varepsilon \mathbb{I}_{bb} - \mathbb{H}'_{bb})^{-1}\mathbb{H}'_{ba}\ , \qquad (5.25)$$

(5.22) reads

$$\overline{\mathbb{H}}_{aa}(\varepsilon) \equiv \mathbb{H}_{aa} + \mathbb{H}'_{aa}(\varepsilon)\ . \qquad (5.26)$$

In what follows, the horizontal asymptotic behavior of the eigenvalues of $\overline{\mathbb{H}}_{aa}(\varepsilon)$ is discussed in Case (1) and Case (2), whereas the vertical behavior is studied in Case (3).

For the horizontal behavior of the eigenvalues of $\overline{\mathcal{H}}_{aa}(\mathcal{E})$ one has

$$\lim_{\mathcal{E}\to\pm\infty} \overline{\mathcal{H}}_{aa}(\mathcal{E}) \equiv \overline{\mathcal{H}}_{aa}(\pm\infty) \equiv \mathcal{H}_{aa} + \delta(\mathcal{E}) \cong \mathcal{H}_{aa}, \qquad (5.27)$$

where δ is a matrix each element of which goes to zero as $\frac{1}{\mathcal{E}}$.

It is well known[13,14,6] that if operators A and B bounded from below have a common domain and satisfy the inequality

$$A \prec B \ , \qquad (5.28)$$

then the eigenvalues of A are smaller than the eigenvalues of B in order from below. Furthermore, we can denote the inequality of the matrices $\mathbb{A}$ and $\mathbb{B}$:

$$\mathbb{A} \prec \mathbb{B} \qquad (5.29)$$

if every diagonal element A_{ii} of $\mathbb{A}$ is less than the corresponding diagonal element of B_{ii} of $\mathbb{B}$, i.e.,

$$A_{ii} < B_{ii} \qquad (5.30)$$

for every arbitrary choice of basis in that domain.

The character of $\overline{\mathcal{H}}_{aa}(\mathcal{E})$ as a function of $\mathcal{E}$ is determined by $\mathcal{H}'_{aa}(\mathcal{E})$. Since the numerator of every diagonal element is greater than or equal to zero, for an arbitrary basis chosen in S(a), the sign of each diagonal element is determined by the sign of corresponding denominator.

Case (1). $-\infty < \mathcal{E} < h_1$

For this case every diagonal element of $\mathcal{H}'(\mathcal{E})$ is negative

for an arbitrary choice of basis in S(a), and the inequality

$$\overline{\mathcal{V}-\mathcal{V}}\,(\mathcal{E}) < \mathcal{V}-\mathcal{V}_{aa} \tag{5.31}$$

is satisfied. Furthermore every diagonal element of $\overline{\mathcal{V}-\mathcal{V}}'_{aa}(\mathcal{E})$ for an arbitrary choice of basis in S(a) becomes smaller as $\mathcal{E}$ increases its value in this range. Consequently, the eigenvalues of $\overline{\mathcal{V}-\mathcal{V}}(\mathcal{E})$ are decreasing monotonically from their corresponding horizontal asymptotes e_1 and e_2 as one increases the value of $\mathcal{E}$. In this sense the horizontal asymptotes are upper bounds to the eigenvalues of $\overline{\mathcal{V}-\mathcal{V}}_{aa}(\mathcal{E})$ for $\mathcal{E} \leq h_1$.

Case (2). $h_5 < \mathcal{E} < +\infty$

For this range of $\mathcal{E}$, every diagonal element of $\mathcal{V}-\mathcal{V}'_{aa}(\mathcal{E})$ for an arbitrary choice of basis in S(a) is positive, giving rise to the inequality

$$\overline{\mathcal{V}-\mathcal{U}}_{aa}(\mathcal{E}) > \mathcal{V}-\mathcal{V}_{aa} \quad , \tag{5.32}$$

and the eigenvalues of $\overline{\mathcal{V}-\mathcal{V}}_{aa}(\mathcal{E})$ are decreasingly monotonically and approach their corresponding horizontal asymptotes e_1 and e_2, respectively. Hence the horizontal asymptotes are lower bounds to the eigenvalues of $\overline{\mathcal{V}-\mathcal{V}}_{aa}(\mathcal{E})$ for $\mathcal{E} > h_5$.

Case (3). $\mathcal{E}$ approaches $h_k (\mathcal{E} \to h_k)$.

In order to facilitate consideration of this limiting case, the operator formalism expressed in (5.8) will be used:

$$\alpha\, \overline{\mathcal{H}}(\mathcal{E})\, \alpha = \alpha\,(\mathcal{H} + \mathcal{H}\, T(\mathcal{E})\, \mathcal{H})\, \alpha \quad , \tag{5.33}$$

where

$$T_{(\mathcal{E})} = \sum_{i=1}^{\infty} \frac{|\Psi_i'><\Psi_i'|}{(\mathcal{E} - h_i)} \quad .$$

For generality, the dimension of S(b) is not restricted but in the present example, Tr(P) = 3. Rearranging (5.8) one obtains

$$\sigma \mathcal{H}(\mathcal{E})\, \sigma = \sigma \left[\left\{ \mathcal{H} + \sum_{\substack{i=1 \\ (i \neq k)}}^{\infty} \frac{\mathcal{H}|\Psi_i'><\Psi_i'|\mathcal{H}}{(\mathcal{E} - h_i)} \right\} + \frac{\mathcal{H}|\Psi_k'><\Psi_k'|\mathcal{H}}{(\mathcal{E} - h_k)} \right] \sigma . \tag{5.34}$$

Defining the operator

$$\Xi_k = \frac{\sigma \mathcal{H}|\Psi_k'><\Psi_k'|\mathcal{H}\sigma}{(\mathcal{E} - h_k)} \quad , \tag{5.35}$$

and denoting its eigenfunction and eigenvalue by $\mathcal{Q}$ and ξ_k,

$$\Xi_k \mathcal{Q} = \xi_k \mathcal{Q} \tag{5.36}$$

one obtains

$$\Xi_k^2 \mathcal{Q} = \xi_k^2 \mathcal{Q} \, , \tag{5.37}$$

$$\Xi_k^2 \mathcal{Q} = \left[\frac{\sigma(\mathcal{H}|\Psi_k'><\Psi_k'|\mathcal{H})\sigma(\mathcal{H}|\Psi_k'><\Psi_k'|\mathcal{H})\sigma}{(\mathcal{E} - h_k)^2} \right] \mathcal{Q}$$

$$= \left[\frac{<\Psi_k'|\mathcal{H}\sigma\mathcal{H}|\Psi_k'>}{(\mathcal{E} - h_k)} \, \Xi_k \right] \mathcal{Q} \quad . \tag{5.38}$$

Combination of (5.37) and (5.38) gives

$$\xi_k \left[\xi_k - \frac{<\Psi_k'|\mathcal{H}\sigma\mathcal{H}|\Psi_k'>}{(\mathcal{E} - h_k)} \right] = 0 ,$$

$$\xi_k = 0 \, ,$$

or

$$\xi_k = \frac{<\Psi_k'|\mathcal{H}\sigma\mathcal{H}|\Psi_k'>}{(\mathcal{E} - h_k)} \quad . \tag{5.39}$$

Therefore Ξ_k has two distinct eigenvalues, zero and $\frac{\langle \Psi'_k | \mathcal{H} \mathcal{O} \mathcal{H} | \Psi'_k \rangle}{(\mathcal{E} - h_k)}$ unless $\mathcal{O}\mathcal{H}\Psi'_k = 0$.

If $\mathcal{O}\mathcal{H}\Psi'_k = 0$, using the relations $P^2 = P$, $\mathcal{O}P = 0$, and $P\Psi'_k = \Psi'_k$, one obtains :

$$0 = [\mathcal{H} - h_k]\Psi'_k = [P\mathcal{H}P - h_k]P\Psi'_k$$
$$= [(\mathcal{O}+P)\mathcal{H} - h_k]P\Psi'_k$$
$$= [\mathcal{H} - h_k]\Psi'_k .$$

Hence Ψ'_k is a simultaneous eigenfunction to $\mathcal{H}$ and $P\mathcal{H}P$ with the eigenvalue h_k. Since the inverse of $P(\mathcal{E} - \mathcal{H})P$ does not exist for $\mathcal{E} = h_k$, the partitioning technique fails. Furthermore h_k is no longer a singular point of (5.34) and (5.35), accordingly there is no asymptotic behavior at $\mathcal{E} = h_k$, and the eigenvalue is lost in this sense. Therefore it will be assumed that $\mathcal{O}\mathcal{H}\Psi'_k \neq 0$. Under this assumption there exists at least one non-zero eigenvalue ξ_k. The eigenvalue ξ_k whether it is zero or non-zero, may be degenerate; however, one can always diagonalize Ξ_k in $S(\mathcal{O})$.

In order to facilitate the following consideration, let the subspace $S(\mathcal{O})$ be divided[19] into orthogonal subspaces $S(\mathcal{O}_a^k)$ and $S(\mathcal{O}_b^k)$ according to the two distinct eigenvalues of Ξ_k, such that

$$\mathcal{O}_a^k \Xi_k = \Xi_k \mathcal{O}_a^k = \mathcal{O}_a^k \Xi_k \mathcal{O}_a^k = \frac{\langle \Psi'_k | \mathcal{H}\mathcal{O}\mathcal{H} | \Psi'_k \rangle}{(\mathcal{E} - h_k)} \mathcal{O}_a^k$$
$$= \frac{\langle \Psi'_k | \mathcal{H}\mathcal{O}_a^k\mathcal{H} | \Psi'_k \rangle}{(\mathcal{E} - h_k)} \qquad (5.40)$$

and

$$\mathcal{O}_b^k \Xi_k = \Xi_k \mathcal{O}_b^k = \mathcal{O}_b^k \Xi \mathcal{O}_b^k = 0 , \tag{5.41}$$

where

$$\mathcal{O} = \mathcal{O}_a^k + \mathcal{O}_b^k , \qquad \mathcal{O}_a^k \mathcal{O}_b^k = \mathcal{O}_b^k \mathcal{O}_a^k = 0 ,$$

$$\mathcal{O}_a^k \mathcal{O} = \mathcal{O}_a^k \mathcal{O} = \mathcal{O}_a^k \quad \text{and} \quad \mathcal{O}_b^k \mathcal{O} = \mathcal{O} \mathcal{O}_b^k = \mathcal{O}_b^k . \tag{5.42}$$

Introducing the relations (5.40, (5.41) and (5.42) into (5.34), one obtains

$$\begin{aligned} \mathcal{O} \bar{\mathcal{H}} \mathcal{O} &= \mathcal{O} [G(\varepsilon) + \Xi_k] \mathcal{O} \\ &= \mathcal{O}_a^k [G(\varepsilon) + \Xi_k] \mathcal{O}_a^k + \mathcal{O}_a^k G(\varepsilon) \mathcal{O}_b^k + \mathcal{O}_b^k G(\varepsilon) \mathcal{O}_a^k \\ &\quad + \mathcal{O}_b^k G(\varepsilon) \mathcal{O}_b^k , \end{aligned} \tag{5.43}$$

where

$$G(\varepsilon) \equiv \mathcal{H} + \sum_{\substack{i=1 \\ (i \neq k)}}^{\infty} \frac{\mathcal{H} |\Psi_i\rangle \langle \Psi_i| \mathcal{H}}{(\varepsilon - h_i)} . \tag{5.44}$$

It is convenient to introduce the operators $\mathcal{S}(\varepsilon)_a$ and $\mathcal{S}(\varepsilon)_b$, by the definitions, as in (3.7):

$$\mathcal{S}(\varepsilon)_a \equiv \mathcal{O}_a^k [\beta \cdot \mathcal{O}_b^k + \mathcal{O}_a^k \{\varepsilon - G(\varepsilon) - \Xi_k\} \mathcal{O}_a^k]^{-1} \mathcal{O}_a^k , \tag{5.45}$$

$$\mathcal{S}(\varepsilon)_b \equiv \mathcal{O}_b^k [\beta \cdot \mathcal{O}_a^k + \mathcal{O}_b^k \{\varepsilon - G(\varepsilon) - \Xi_k\} \mathcal{O}_b^k]^{-1} \mathcal{O}_b^k , \tag{5.46}$$

where β is an arbitrary non-zero number.

In the following we will simply use the symbolic notation

$$\mathcal{S}(\varepsilon)_a = \frac{\mathcal{O}_a^k}{[\varepsilon - G(\varepsilon) - \Xi_k]} \tag{5.47}$$

$$\mathcal{S}(\varepsilon)_b = \frac{\mathcal{O}_b^k}{[\ \varepsilon - G(\varepsilon)\ ]} \quad . \tag{5.48}$$

In order to observe the asymptotic behavior of $\mathcal{O}\bar{\mathcal{H}}\mathcal{O}$ as ε approaches h_k, one can contract $\mathcal{O}\bar{\mathcal{H}}\mathcal{O}$ with respect to the subspace $S(\mathcal{O}_b^k)$ and $S(\mathcal{O}_a^k)$, respectively, using (5.43) and (5.44), one obtains (cf.(3.17))

$$\mathcal{O}_b^k \bar{G}_b \mathcal{O}_b^k = \mathcal{O}_b^k G(\varepsilon) \mathcal{O}_b^k + \mathcal{O}_b^k G(\varepsilon) \mathcal{S}(\varepsilon)_a G(\varepsilon) \mathcal{O}_b^k \ , \tag{5.49}$$

$$\mathcal{O}_a^k \bar{G}_a \mathcal{O}_a^k = \mathcal{O}_a^k G(\varepsilon) \mathcal{O}_a^k + \mathcal{O}_a^k G(\varepsilon) \mathcal{S}(\varepsilon)_b G(\varepsilon) \mathcal{O}_a^k \ , \tag{5.50}$$

where

$$\bar{G}_b = \mathcal{O}\bar{\mathcal{H}}\mathcal{O} + \mathcal{O}\bar{\mathcal{H}}\mathcal{S}(\varepsilon)_a \bar{\mathcal{H}}\mathcal{O}, \tag{5.51}$$

$$\bar{G}_a = \mathcal{O}\bar{\mathcal{H}}\mathcal{O} + \mathcal{O}\bar{\mathcal{H}}\mathcal{S}(\varepsilon)_b \bar{\mathcal{H}}\mathcal{O}. \tag{5.52}$$

As ε approaches h_k, Ξ_k becomes enormously large, which makes the operator $\mathcal{S}_a(\varepsilon)$ go to zero. Hence one has the results

$$\lim_{\varepsilon \to h_k} \mathcal{O}_b^k \bar{G}_b \mathcal{O}_b^k \cong \mathcal{O}_b^k G(\varepsilon) \mathcal{O}_b^k \ , \tag{5.53}$$

$$\lim_{\varepsilon \to h_k} \mathcal{O}_a^k \bar{G}_a \mathcal{O}_a^k \cong \mathcal{O}_a^k \Xi_k \mathcal{O}_a^k = \frac{\langle \Psi_k' | \mathcal{H} \mathcal{O}_a^k \mathcal{H} | \Psi_k' \rangle}{(\varepsilon - h_k)} \ . \tag{5.54}$$

These give the theorem that, if ε approaches one of the eigenvalues of $P\mathcal{H}P$, say h_k, where h_k is not an eigenvalue of $\mathcal{H}$, the n_b eigenvalues, where $n_b = \mathrm{Tr}(\mathcal{O}_b^k)$, of $\mathcal{O}\bar{\mathcal{H}}\mathcal{O}$ approach the eigenvalues of $\mathcal{O}_b^k\, G(\varepsilon)\, \mathcal{O}_b^k$ and the n_a eigenvalues, where $n_a = \mathrm{Tr}(\mathcal{O}_a^k)$, of $\mathcal{O}\bar{\mathcal{H}}\mathcal{O}$ become infinite with the order of magnitude $\dfrac{\langle \Psi_k' | \mathcal{H} \mathcal{O}_a^k \mathcal{H} | \Psi_k' \rangle}{(\varepsilon - h_k)}$.

In concluding the discussion in connection with Figure 1, the way of estimating lower bounds to the ground state will be studied in connection with (3.18).

Theorem 5.2. If E_1 is the ground state energy of $\mathcal{H}$ and the eigenfunction of the ground state is not orthogonal to $S(\alpha)$, then the lowest eigenvalue of $\tilde{\mathcal{H}}(E_1)$ is E_1.

Proof: By corollary 5.1, $\tilde{\mathcal{H}}(E_1)$ has at least one eigenvalue which is equal to E_1. If one denotes the eigenvalues of $\tilde{\mathcal{H}}(E_1)$ by $\tilde{E}_1, \tilde{E}_2, \ldots$, in order and assumes that

$$E_1 = \tilde{E}_k, \qquad k > 1, \tag{5.55}$$

then by the variation principle one has

$$E_1 \leq h_1 \quad ,$$

where h_1 is the ground state eigenvalue of $P\mathcal{H}P$. Since the cases where the eigenvalues of $\mathcal{H}$ are equal to the eigenvalues of $P\mathcal{H}P$, are excluded from consideration, one may assume that $E_1 < h_1$, then by (5.55)

$$\tilde{E}_k < h_1 \quad . \tag{5.56}$$

Now consider

$$\tilde{\mathcal{H}}(\tilde{E}_k) = \alpha \bar{\mathcal{H}}(\tilde{E}_k)\alpha = \alpha\left[\mathcal{H} + \sum_{i=1}^{\infty} \frac{\mathcal{H}|\Psi_i'\rangle\langle\Psi_i'|\mathcal{H}}{(\tilde{E}_k - h_i)}\right]\alpha. \tag{5.57}$$

The term $\sum_{i=1}^{\infty} \frac{\mathcal{H}|\Psi_i'\rangle\langle\Psi_i'|\mathcal{H}}{(\tilde{E}_k - h_i)}$ in (5.57) is negative definite by the inequality in (5.56), therefore if one considers the range $\tilde{E}_{k-1} < \varepsilon < \tilde{E}_k$,

then

$$\tilde{\mathcal{H}}(E_1) = \tilde{\mathcal{H}}(\tilde{E}_k) < \mathcal{H}(\varepsilon) \quad , \tag{5.58}$$

and it follows[13,14] that

$$\tilde{E}_i < \varepsilon_i \qquad (i=1,2,..,\mathrm{Tr}(\mathcal{O})) \ , \tag{5.59}$$

where ε_i is the i^{th} eigenvalues of $\tilde{\mathcal{H}}(\varepsilon)$. While decreasing ε continually from $\tilde{E}_k$ to $\tilde{E}_{k-1}$ each ε_i will increase in magnitude continuously, and it will finally reach the point where ε_{k-1}, which is greater than E_{k-1}, is equal to ε. Then by theorem 5.1, the ε at this point ($\varepsilon = \varepsilon_{k-1}$) is an eigenvalue of $\mathcal{H}$, however $\varepsilon < \tilde{E}_k = E_1$ and this contradicts the assumption that $\tilde{E}_k = E_1$ if $k > 1$. Q.E.D.

One may assume that the Hamiltonian $\mathcal{H}$ can be written in the form

$$\mathcal{H} = \mathcal{H}^o + V$$

where $\mathcal{H}^o$ has known eigenvalues and eigenfunctions and V is positive definite. It is further assumed that $\mathcal{H}^o$ has discrete energy levels

$$E_1^o \leq E_2^o \leq \cdots \ , \tag{5.60}$$

below its continuous spectrum. The corresponding orthonormalized eigenfunctions are denoted by Ψ_i^o, so that

$$\mathcal{H}^o \Psi_i^o = E_i^o \Psi_i^o \quad , \ \langle \Psi_i^o | \Psi_j^o \rangle = \delta_{ij} \ . \tag{5.61}$$

If the projection operator in (3.5) is associated with the functions Ψ_i^o by

$$\mathcal{O} = \sum_{i=1}^{g} |\Psi_i^o\rangle\langle\Psi_i^o| \quad , \tag{5.62}$$

the introduction of (5.61) into (3.14) leads to the form

$$E\mathcal{O}\phi = \mathcal{O}(\mathcal{H}^{o} + V + VT(E)V)\mathcal{O}\phi. \tag{5.63}$$

It is convenient to introduce the generalized reduced resolvent T_o and the reaction operator t for the multi-dimensional reference manifold by the relations

$$T_o(\mathcal{E}) \equiv \frac{P}{\mathcal{E} - \mathcal{H}^{o}} \quad , \tag{5.64}$$

$$t(\mathcal{E}) \equiv V + VT(\mathcal{E})V \quad . \tag{5.65}$$

Then using the operator identity

$$(A-B)^{-1} = A^{-1} + A^{-1}B(A-B)^{-1} \quad , \tag{5.66}$$

it can be shown[6] that

$$t^{-1} = V^{-1} - T_o \tag{5.67}$$

provided V^{-1} exists.

The condition which makes $T_o(\mathcal{E})$ negative definite will be the sufficient condition for $t^{-1}(\mathcal{E})$ and $t(\mathcal{E})$ to be positive definite. If the variable $\mathcal{E}$ is below the continuous spectrum of $\mathcal{H}^{o}$ with the relation

$$E_k^o < \mathcal{E} < E_{k+1}^o \quad , \tag{5.68}$$

then $T_o(\mathcal{E})$ is negative definite if one uses the projection operator defined by

$$\mathcal{O} = \sum_{i=1}^{\ell} |\Psi_i^o\rangle\langle\Psi_i^o| \quad , \tag{5.69}$$

where $\ell \geq k$. This gives

$$t > 0 \quad , \tag{5.70}$$

and by means of the inner projection defined in (4.3) one obtains

$$t' = t^{\frac{1}{2}} Q^n t^{\frac{1}{2}} \quad , \tag{5.71}$$

so that

$$t'(\mathcal{E}) \leq t(\mathcal{E}) \quad . \tag{5.72}$$

In order to consider the bracketing property for an eigenvalue E of the Hamiltonian $\mathcal{H}$, in a multi-dimensional reference manifold, consider (3.14) and define a function $f(\mathcal{E})$ by

$$f(\mathcal{E}) = \frac{\langle \phi | \Theta(\mathcal{H} + \mathcal{H} T_{(\mathcal{E})} \mathcal{H}) \Theta | \phi \rangle}{\langle \phi | \Theta | \phi \rangle} \quad , \tag{5.73}$$

then

$$\frac{\partial f(\mathcal{E})}{\partial \mathcal{E}} = - \frac{\langle \phi | \Theta(\mathcal{H} T^2_{(\mathcal{E})} \mathcal{H}) \Theta | \phi \rangle}{\langle \phi | \Theta | \phi \rangle} < 0 \quad . \tag{5.74}$$

It is seen from (5.74) that for a properly chosen reference function ϕ, which satifies (3.14), the bracketing theorem holds[12], hence there will be at least one eigenvalue E of $\mathcal{H}$ between $\mathcal{E}$ and $f(\mathcal{E})$. therefore if $\mathcal{E}_o$ is an upper bound to the eigenvalue E and if both E and $\mathcal{E}_o$ are between two consecutive distinct eigenvalues of $P\mathcal{H}P$ [*7], then $f(\mathcal{E}_o)$ is a lower bound to E:

$$\mathcal{E}_1 \equiv f(\mathcal{E}_o) < E < \mathcal{E}_o \quad . \tag{5.75}$$

The first order iteration procedure using this bracketing property will be convergent if $|\frac{\partial f}{\partial \mathcal{E}}| < 1$ and divergent if $|\frac{\partial f}{\partial \mathcal{E}}| > 1$.

[*7] Note that the common eigenvalues of $\mathcal{H}$ and $P\mathcal{H}P$, if they exist, are eliminated.

Assume that Ψ_1 denotes the ground state eigenfunction of $\mathcal{H}$ with the eigenvalue E_1 and further assume that $\mathcal{E}_o$, an upper bound to E_1, is lower than the lowest eigenvalue of $P\mathcal{H}P$ which is not a simultaneous eigenvalue of $\mathcal{H}$. If $\mathcal{E}_o$ satisfies the relation

$$E_p < \mathcal{E}_o < E_{p+1} \quad ,$$

then the introduction of a projection operator of the form (cf. (5.69))

$$\mathcal{O} = \sum_{i=1}^{g} |\Psi_i^o\rangle\langle\Psi_i^o| \quad , \qquad (\text{where } g \geq p) \tag{5.76}$$

makes the reaction operator $t(\mathcal{E}_o)$ positive definite. Hence all eigenfunctions of $\mathcal{H}^o$ associated with the eigenvalues less than the upper bound $\mathcal{E}_o$ are included in the set $\{\Psi_1^o, \Psi_2^o, \ldots, \Psi_p^o, \ldots, \Psi_g^o\}$. Let us define ϕ_1 by the relation

$$\phi_1 = \mathcal{O}\Psi_1 \quad , \tag{5.77}$$

where $\mathcal{O}$ is given by (5.76). Using the definition (5.77) and relations (5.63), (5.65) and (5.73), one can write

$$f(\mathcal{E}_o) = \langle\phi_1|\mathcal{H}^o + t(\mathcal{E}_o)|\phi_1\rangle / \langle\phi_1|\phi_1\rangle \quad . \tag{5.78}$$

For this case the relation in (5.75) may be replaced by

$$\mathcal{E}_1 < E_1 < \mathcal{E}_o \tag{5.79}$$

Defining $\mathcal{E}_1'$ by

$$\mathcal{E}_1' \equiv \langle\phi_1|\mathcal{H}^o + t'(\mathcal{E}_o)|\phi_1\rangle / \langle\phi_1|\phi_1\rangle, \tag{5.80}$$

and noting the relations (5.72) and (5.79) one obtains the following inequality:

$$\mathcal{E}_1' \leq \mathcal{E}_1 < E_1 < \mathcal{E}_o \quad . \tag{5.81}$$

Since ϕ_1 is not known, one minimizes the operator $\mathcal{H}''$,

$$\mathcal{H}'' = \mathcal{P}\mathcal{H}^{o} + t'(\mathcal{E}_o) \quad , \tag{5.82}$$

in $S(\mathcal{O})$ to obtain some value less than $\mathcal{E}_1'$.

Denoting the lowest eigenvalue of $\mathcal{H}''$ in $S(\mathcal{O})$ by $\mathcal{E}_1''$, one obtains

$$\mathcal{E}_1'' \leq \mathcal{E}_1' \quad . \tag{5.83}$$

Then it is seen that $\mathcal{E}_1''$ is given by the lowest eigenvalue of the Hermitian matrix

$$\begin{pmatrix} E_1^o + t_{11}' & t_{12}' & \cdots & t_{1g}' \\ t_{21}' & E_2^o + t_{22}' & \cdots & t_{2g}' \\ \cdot & \cdot & \cdots & \cdot \\ t_{g1}' & t_{g2}' & \cdots & E_g^o + t_{gg}' \end{pmatrix} \quad . \tag{5.84}$$

Combining (5.79) and (5.83) one obtains

$$\mathcal{E}_1'' \leq \mathcal{E}_1' \leq E_1 < \mathcal{E}_o \quad . \tag{5.85}$$

This method will be applied in Chapter VII in the estimation of the lower bound to the ground state energy of two-electron isoelectronic series.

CHAPTER VI

THE STARK EFFECT IN THE RIGID ROTATOR

In this chapter, lower bounds to the energy eigenvalues for the rigid rotator in a uniform electric field (the Stark effect) are calculated using the method described in Chapter IV. For the inner projection of the positive perturbation V, the Aronszajn space $\mathcal{J}$ is used, where $\mathcal{J}$ consists of the eigenfunctions Ψ_i^o of $\mathcal{H}^o$ and has to satisfy the condition given by (4.27). The notation is consistent with that of Chapter IV. The equation used in this chapter for the calculation of lower bounds is (3.34) with t' expressed by (4.26):

$$\mathcal{E}_1' = \langle\bar{\Psi}|\mathcal{H}^o|\Psi\rangle + \langle\bar{\Psi}|V|\mathcal{J}\rangle\langle\mathcal{J}|V - VT_oV|\mathcal{J}\rangle^{-1}\langle\mathcal{J}|V|\bar{\Psi}\rangle. \quad (6.1)$$

In a problem where V is a positive perturbation with a constant coefficient K as a strength parameter, one can write

$$V = KU \quad . \quad (6.2)$$

For this case one obtains

$$\mathcal{E}_1' = \langle\bar{\Psi}|\mathcal{H}^o|\bar{\Psi}\rangle + \beta^+ B^{-1}\beta \quad , \quad (6.3)$$

where

$$B = \langle\mathcal{J}|U/K - UT_oU|\mathcal{J}\rangle \quad , \quad (6.4)$$

$$\beta = \langle\mathcal{J}|U|\bar{\Psi}\rangle \quad . \quad (6.5)$$

If φ is an eigenfunction of $\mathcal{H}^{\circ}$, then

$$\overline{\varphi} = \varphi \quad . \tag{6.6}$$

The wave equation for the rigid rotator consisting of two mass points m_1 and m_2, which are separated by fixed distance R, is

$$\frac{\hbar^2}{2MR^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi^{\circ}(\theta,\phi)+W\Psi^{\circ}(\theta,\phi)=0, \tag{6.7}$$

where W is the rotational energy and M is the reduced mass of m_1 and m_2, i.e.,

$$M = (m_1m_2)/(m_1+m_2) \quad . \tag{6.8}$$

Let

$$-\omega(\theta,\phi) = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \quad , \tag{6.9}$$

and

$$(2MR^2\omega)/\hbar^2 = E^{\circ} \quad , \tag{6.10}$$

where ω is the Hamiltonian in dimensionless units and E° is the corresponding energy. If $\Psi^{\circ}_{\ell m}$ denotes the normalized wave function given by[20]

$$\Psi^{\circ}_{\ell m} = \left[\frac{2\ell+1}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}\right] P_{\ell}^{|m|}(\cos\theta)\, e^{im\phi} \tag{6.11}$$

where $P_{\ell}^{m}(\cos\theta)$ is the associated Legendre polynomial, then (6.7) reads simply

$$\omega(\theta,\phi)\Psi^{\circ}_{\ell,m}(\theta,\phi) = E^{\circ}_{\ell}\,\Psi^{\circ}_{\ell,m}(\theta,\phi) \quad ,$$

or

$$\omega(\theta,\phi)Y^{o}_{\ell,m}(\theta,\phi) = \ell(\ell+1)Y^{o}_{\ell,m}(\theta,\phi) \quad . \tag{6.12}$$

The rigid rotator of dipole moment μ in a uniform electric field F is characterized by the wave equation of the form

$$\mathcal{H}\Psi = E\Psi \quad , \tag{6.13}$$

with $$\mathcal{H} = \omega + K\cdot\cos\theta \quad ,$$

and $$K = (2uFMR^{2})/\hbar^{2} \quad . \tag{6.14}$$

In order that the perturbation V in (6.2) shall be positive definite, we shall write

$$\mathcal{H}^{o} = \omega - K \quad , \tag{6.15}$$

$$V = K(1 + \cos\theta) \quad , \tag{6.16}$$

and

$$U = 1 + \cos\theta \quad . \tag{6.17}$$

Then this division of $\mathcal{H}$ into an unperturbed and a perturbed part gives

$$\mathcal{H} = \mathcal{H}^{o} + KU \tag{6.18}$$

with

$$U > 0 \quad . \tag{6.19}$$

For this case, the Schrödinger equation reads

$$[\omega(\theta,\phi) + K \cos\theta]\Psi(\theta,\phi) = E\Psi(\theta,\phi) \quad . \tag{6.20}$$

This equation is easily seen to be separable with respect to the variables Θ and ϕ, so we can write the eigenfunction in the product form

$$\Psi(\theta,\phi) = Z(\theta)\cdot \Phi(\phi) \quad , \tag{6.21}$$

with [*8] $\quad \Phi(\phi) = \left(\frac{1}{2\pi}\right) e^{\pm im\phi} \quad ,$ where $m = 0, 1, 2, \ldots;$

and $$Z(\theta) = \sum_{i=0}^{\infty} C_i \, P^m_{i+m}(\cos\theta) \quad , \tag{6.22}$$

where $P^m_\ell(\Theta)$ is an associated Legendre polynomial.

Since the space with which we are concerned can be subdivided according to the value of m, we can treat the problem separately for each subspace. The normalized reference function ϕ in (6.1) is arbitrary; however, in order to make the first order iteration of (6.1) convergent, the condition[6]

$$\langle T\mathcal{H}\varphi \mid T\mathcal{H}\varphi\rangle \;<\; \langle\varphi\mid\varphi\rangle \tag{6.23}$$

must be satisfied. The left side of this inequality approaches zero as K approaches zero for a fixed reference function only if ϕ is an eigenfunction of $\mathcal{H}^0$; therefore it seems reasonable to make this

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[*8] Except for the case m = 0, we have doubly degenerate eigenstates, so we will consider only the absolute value of m.

choice for ϕ provided K is small. Thus in the subspace m, we have for the ℓ^{th} excited state,

$$\varphi = Y_\ell^m(\theta,\phi) = N_\ell^m P_\ell^m(\cos\theta)\, e^{im\phi} \tag{6.24}$$

where $Y_\ell^m(\theta,\phi)$ is the normalized "spherical harmonics" and where N_ℓ^m is the normalization factor for the spherical harmonics $Y_\ell^m(\theta,\phi)$ given by

$$N_\ell^m = \left[\frac{(\ell-m)!(2\ell+1)}{(\ell+m)!\ 4\pi}\right] \quad . \tag{6.25}$$

Lower bounds $\mathcal{E}_1'$ for the energy levels can be calculated by use of (6.3) through (6.5) with $\mathcal{E}_o$ in T_o obtained from a variation calculation. The Aronszajn space which satisfies the condition of (4.27) is given by $\mathcal{S} = (g_1, g_2, \ldots, g_i, \ldots, g_n)$,

with $$g_i = Y_{m+i-1}^m(\theta,\phi) \tag{6.26}$$

Since $U = 1 + \cos\theta$,

$$\beta_i = \langle g_i | U | Y_\ell^m \rangle = \langle Y_{m+i-1}^m | (1+\cos\theta) | Y_\ell^m \rangle \, . \tag{6.27}$$

Using the recurrence relation

$$(\cos\theta)P_\ell^m = (2\ell+1)^{-1}[(\ell+1-m)P_{\ell+1}^m + (\ell+m)P_{\ell-1}^m] \quad , \tag{6.28}$$

one obtains

$$\beta_i = \left[\frac{(\ell+1-m)(\ell+1+m)}{(2\ell+1)(2\ell+3)}\right]^{\frac{1}{2}} \delta_{m+i-1,\ell+1} + \delta_{m+i-1,\ell} + \left[\frac{(\ell+m)(\ell-m)}{(2\ell+1)(2\ell-1)}\right]^{\frac{1}{2}} \delta_{m+i-1,\ell-1} \; ;$$

therefore

$$\beta_i = \left[\frac{(\ell+1-m)(\ell+1+m)}{(2\ell+1)(2\ell+3)}\right] \qquad \text{for } i = \ell+2-m,$$

$$\beta_i = 1 \qquad \text{for } i = \ell+1-m,$$

$$\beta_i = \left[\frac{(\ell+m)(\ell-m)}{(2\ell+1)(2\ell-1)}\right] \qquad \text{for } i = \ell-m, \tag{6.29}$$

$$\beta_i = 0 \qquad \text{otherwise,}$$

and $$\langle \varphi | \mathcal{L}^2 | \varphi \rangle = \langle Y_\ell^m | (\omega - K) | Y_\ell^m \rangle = \ell(\ell+1) - K \quad . \tag{6.30}$$

In order to have at least one non-zero element for β_i, as we can see from (6.29), n must be at least as large as $(\ell-m)$; otherwise

$$\mathcal{E}_1' = \ell(\ell+1) - K \quad , \tag{6.31}$$

which is trivial.

For the calculation of matrix elements of $\mathcal{B}$, we consider

$$B_{ij} = \langle g_i | (U/K) - U T_o U | g_j \rangle \quad . \tag{6.32}$$

Let $$F_i = T_o U g_i \tag{6.33}$$

$$= \frac{P}{(\mathcal{E}_o - \mathcal{L}^2)} (1 + \cos\theta) Y_{m+i-1}^m \quad , \tag{6.34}$$

where $$P = 1 - |\varphi\rangle\langle\varphi| = 1 - |Y_\ell^m\rangle\langle Y_\ell^m| \quad .$$

Using (6.28), we obtain

$$F_i = \sum_{K=i-1}^{i+1} D_K \, Y_{m+K-1}^m \quad , \tag{6.35}$$

with

$$D_{i-1} = \frac{1}{[\mathcal{E}_o - (i+m-2)(i+m-1)+K]} \left[\frac{(i-1)(i-2m+1)}{(2i+2m-1)(2i+2m-3)}\right]^{\frac{1}{2}}$$

$$= 0 \qquad (\text{if } \ell = i+m-2) \tag{6.36}$$

$$D_i = \frac{1}{[\mathcal{E}_o - (i+m-1)(i+m)+K]} = 0, \qquad (\text{if } \ell = i+m-1) \tag{6.37}$$

$$D_{i+1} = \frac{1}{[\mathcal{E}_o-(i+m)(i+m+1)]} \left[\frac{i(i+2m)}{(2i+2m-1)(2i+2m+1)}\right]^{\frac{1}{2}} \tag{6.38}$$

$$= 0, \qquad (\text{if } \ell = i+m).$$

Note that the reason D_i vanishes for certain values of i is that F_i is orthogonal to Y_ℓ^m.

Introducing (6.33) into (6.32),

$$B_{ki} = \langle g_k|(U/K)|g_i\rangle - \langle g_k|U|F_i\rangle . \tag{6.39}$$

Then, the non-vanishing matrix elements of $\mathbb{B}$ are

$$B_{i+2,i} = \left[\frac{-1}{\{\mathcal{E}_o - (i+m)(i+m+1)+K\}(i+2m+1)}\right]\left[\frac{i(i+1)(i+2m)(i+2m+1)}{(2i+2m-1)(2i+2m+3)}\right]^{\frac{1}{2}};$$

$$B_{i+1,i} = \left[\frac{1}{K} - \left\{\frac{1}{\mathcal{E}_o - (i+m)(i+m+1)+K}\right\} - \left\{\frac{1}{\mathcal{E}_o - (i+m-1)(i+m)+K}\right\}\right]$$

$$\left[\frac{i(i+2m)}{(2i+2m+1)(2i+2m-1)}\right]^{\frac{1}{2}};$$

$$B_{i,i} = \frac{1}{K} - \left[\frac{i(i+2m)}{\{\mathcal{E}_o - (i+m)(i+m+1)+K\}(2i+2m-1)(2i+2m+1)}\right] - \left[\frac{1}{\mathcal{E}_o-(i+m-1(i+m)+K}\right]$$

$$- \left[\frac{(i-1)(i-1+2m)}{\{\mathcal{E}_o - (i+m-2)(i+m-1)+K\}(2i+2m-1)(2i+2m-3)}\right]$$

$$B_{i-1,i} = \left[\frac{1}{K} - \left\{\frac{1}{\mathcal{E}_o - (i+m-1)(i+m)+K}\right\} - \left\{\frac{1}{\mathcal{E}_o - (i+m-2)(i+m-1)+K}\right\}\right]$$

$$\left[\frac{(i-1)(i+2m-1)}{(2i+2m-1)(2i+2m-3)}\right]^{\frac{1}{2}};$$

$$B_{i-2,i} = \left[\frac{-1}{\{\mathcal{E}_o - (i+m-2)(i+m-1)+K\}(2i+2m-3)}\right]\left[\frac{(i-1)(i-2)(i+2m-1)(i+2m-2)}{(2i+2m-1)(2i+2m-3)}\right]^{\frac{1}{2}}. \tag{6.40}$$

Equations (6.29), (6.30) and (6.40) give us the necessary matrix elements for calculation of lower bounds expressed by (6.3). It is easily seen that

$$B_{i+2,i} = B_{i,i+2} \quad \text{and} \quad B_{i+1,i} = B_{i,i+1} \ .$$

If we change the Hamiltonian in (6.13) to

$$\mathcal{H} = \omega - K \cos\theta \tag{6.41}$$

we would expect the same result since we only reversed the uniform electric field. The algebraic identity of these two cases has been demonstrated as a partial check on the algebra.

Upper and Lower Bounds for the Rigid-Rotator--Numerical Results

The entire calculation was done on the IBM 709 at the University of Florida Computing Center. Upper Bound energies were first obtained by the Rayleigh-Ritz variational method using subroutine Givens[*9] (single precision). In order to clarify the cases where the upper bound and lower bound were so close that it was difficult to say which was lower, the upper bounds were refined using a double-precision iteration method[*10], and the remainder of the calculation was also carried out in double precision.

[*9] "Eigenvalues and Eigenvectors by the Givens Method," Quantum Chemistry Program Exchange, QCPE 12C (1963).

[*10] C. E. Reid, "Eigenvalues by Löwdin's Partitioning Method," QCPE 14C (1963), modified for double precision.

Except for the level m = 0, all the other levels are degenerate. However, the Hamiltonian $\mathcal{H}$ commutes with $L_z = \frac{\hbar}{i}\frac{\partial}{\partial \phi}$; therefore one can separately solve the energy eigenvalue problem for each subspace S_m for a given value m of L_z. Calculations for the first six subspaces (S_o to S_5) have been carried out for the twenty lowest eigenvalues in each subspace with the perturbation coefficient K ranging from 0.1 to 1.0.

In Table 1, upper bounds $E_U = \varepsilon_o$ and lower bounds $E_L = \varepsilon_1'$ of energy eigenvalues are given to sixteen significant digits for typical choices of K and m. The eigenvalues are labeled by the ℓ of the unperturbed state.

N_U is the number of basis functions used for finding upper bounds (these functions are the normalized spherical harmonics Y_m^m, Y_{m+1}^m, ... $Y_{m+N_U-1}^m$), and N_L is the number of basis functions Y_m^m, Y_{m+1}^m, ... $Y_{m+N_L-1}^m$) for the Aronszajn space.

This method of evaluating lower bounds, using the bracketing property of (6.1), requires good upper bounds, and the upper bounds are improved by increasing the number of basis functions N_U used in the variational calculation. The results in Table 1 indicate that fairly good upper bounds are generally obtained by taking $N_U = \ell + 5$. In order to obtain good lower bounds, we have to enlarge the Aronszajn space, and we can see from the results indicated in Table 1 that in the present case the dimension of the Aronszajn space N_L is sufficient to give good lower bounds provided $N_L = \ell + 5$.

TABLE 1

UPPER AND LOWER BOUNDS FOR EIGENVALUES FOR THE STARK EFFECT IN A RIGID ROTATOR

m = 0,			K = 0.5
ℓ	N_U	N_L	E_U and E_L [a]
0	5		-0.4105079348229 97
		5	-0.4105079348230 94
1	6		2.024369028254599
		6	2.024369028254599
2	7		6.005966607238925
		7	6.005966607238923
3	8		12.00277843867649
		8	12.00277843867648
4	9		20.00016234906589
		9	20.00016234906587
5	10		30.00106840547832
		10	30.00106840547831
6	11		42.00075758568145
		11	42.00075758568144
7	12		56.00056561485280
		12	56.00056561485278
8	13		72.00043859831220
		13	72.00043859831218
9	14		90.00003501409683
		14	90.00003501409682
10	15		110.0002860416819
		15	110.0002860416819
11	16		132.0002380955195
		16	132.0002380955193
12	17		156.0002012884138
		17	156.0002012884136
13	18		182.0001724138988
		18	182.0001724138987
14	19		210.0001493429597
		19	210.0001493429596
15	20		240.0001306165556
		20	240.0001306165555
16	20		272.0001152074046
		20	272.0001152074045

TABLE 1--Continued

m = 0,			K = 0.5
ℓ	N_U	N_L	E_U and E_L [a]
17	20		306.0001023751246
		20	306.0001023751242
18	20		342.0000916098325 [b]
		20	342.0000915749897
		23	342.0000915751040
19	20		380.0016458519702
		20	380.0000722250626
		24	380.0000822706509
m = 1,			K = 1.0
1	5		1.950333905229181
		5	1.950333905229141
2	6		6.011577927242672
		6	6.011577927242670
3	7		12.008326144358 40
		7	12.008326144358 39
4	8		20.00551933162358
		8	20.00551933162356
5	9		30.00384626739139
		9	30.00384626739157
6	10		42.00281392300602
		10	42.00281392300600
7	11		56.00214127777589
		11	56.00214127777586
8	12		72.00168130591093
		12	72.00168130591091
9	13		90.00135388552912
		13	90.00135388552910
10	14		110.0011129663826
		14	110.0011129663825
11	15		132.0009307395922
		15	132.0009307395921
12	16		156.0007896715423
		16	156.0007896715422
13	17		182.0006782886897
		17	182.0006782886897

TABLE 1--Continued

m = 1,			K = 1.0
ℓ	N_U	N_L	E_U and E_L [a]
14	18		210.0005888386502
		18	210.0005888386500
15	19		240.0005159358681
		19	240.0005159358679
16	20		272.0004557472937
		20	272.0004557472681
17	20		306.0004054860207
		20	306.0004054860206
18	20		342.0003630874514
		20	342.0003630874365
		23	342.0003630874366
19	20		380.0003274705419
		20	380.0003269927098
		23	380.0003269958156
20	20		420.0062377999262
		20	420.0002179895039
		24	420.0002942543069
m = 3			K = 0.7
3	5		11.993196489724 68
		5	11.993196489724 67
4	6		19.998884864220 10
		6	19.998884864220 10
5	7		30.000209012900 87
		7	30.000209012900 86
6	8		42.000530196452 72
		8	42.000530196452 71
7	9		56.000574062148 88
		9	56.000574062148 87
8	10		72.000537269508 79
		10	72.000537269508 75
9	11		90.000480388062 58
		11	90.000480380625 6
10	12		110.00042302735 25
		12	110.00042302735 23

TABLE 1--Continued

m = 3,			K = 0.7
ℓ	N_U	N_L	E_U and E_L [a]
11	13		132.0003712115186
		13	132.0003712115184
12	14		156.0003262415718
		14	156.0003262415716
13	15		182.0002877983403
		15	182.0002877983402
14	16		210.0002550776513
		16	210.0002550776511
15	17		240.0002272074346
		17	240.0002272074345
16	18		272.0002033918627
		18	272.0002033918626
17	19		306.0001829503520
		19	306.0001829503519
18	20		342.0001653171585
		20	342.0001653172584
19	20		380.0001500277721
		20	380.0001500277720
20	20		420.0001367024596
		20	420.0001367024584
21	20		462.0001251239667
		20	462.0001250304234
22	20		506.0027336495416
		20	506.0000914202348

m = 5,			K = 1.0
5	5		29.99359063883720
		5	29.99359063883718
6	6		41.99761861361275
		6	41.99761861361275
7	7		55.99923213730367
		7	55.99923213730366
8	8		71.9999267874087l
		8	71.9999267874086 9
9	9		90.00023337531917
		9	90.00023337531912

TABLE 1--Continued

m = 5,			K = 1.0
ℓ	N_U	N_L	E_U and E_L [a]
10	10		110.0003640283063
		10	110.0003640283062
11	11		132.0004112436340
		11	132.0004112436339
12	12		156.0004180542290
		12	156.0004180542288
13	13		182.0004054534825
		13	182.0004054534824
14	14		210.0003840228910
		14	210.0003840228908
15	15		240.0003591944730
		15	240.0003591944728
16	16		272.0003337620168
		16	272.0003337620166
17	17		306.0003091323675
		17	306.0003091323674
18	18		342.0002859711714
		18	342.0002859711713
19	19		380.0002645455813
		19	380.0002645455812
20	20		420.0002449100770
		20	420.0002449100769
21	20		462.0002270087367
		20	462.0002270087364
22	20		506.0002107319706
		20	506.0002107319655
23	20		552.0001962023146
		20	552.0001959463010
24	20		600.0049841862676
		20	600.0001226802245

[a]The upper bound is given first, followed by the lower bound.

[b]In those cases where more than one N_L was used, a lower bound is indicated for each N_L.

Upper and lower bounds agree to fourteen significant digits[*11] in those cases where $N_U = N_L = \ell + 5$. For the highest energy levels listed, for example, K = 1.0, m = 1, $\ell = 20$, $N_U = 20$, $N_L = 20$, the agreement is poorer, but is improved somewhat by increasing N_L. The limitation here seems to be due to the poorness of the upper bound rather than the dimension of the Aronszajn space.

To see in more detail the effect of N_L for a fixed value of N_U, several examples are given in Table 2. It is seen from (6.29) that, when the Aronszajn space $\mathcal{G}$ is chosen as indicated in (6.26), for N_L less than $(\ell-m)$, the lower bound E_U is a persistent lower bound, given by

$$E_L = \ell(\ell+1) - K \ .$$

In order to obtain better lower bounds, therefore, the Aronszajn space $\mathcal{G}$ has to be chosen in such a way that there are non-vanishing elements of β_i; namely $B_{\ell-m}$, $\beta_{\ell-m+1}$, and $\beta_{\ell-m+2}$ in our case. Increasing N_U in Table 2 beyond the values indicated did not improve the lower bound.

[*11] Except for one case, m = 0, $\ell = 0$, K = 0.5, where it agrees only for 13 significant figures.

TABLE 2

EFFECT OF N_L ON E_L IN THE CONVERGENCE TO THE EIGENVALUE

m	K	ℓ	N_U	N_L	E_U and E_L
0	0.1	10	15		110.0000114416483
				1-9[a]	109.9000000000000*[b]
				10	109.9477443614383
				13	110.0000114416482
0	0.5	10	15		110.0002860416819
				1-9	109.5000000000000*
				10	109.7412282838218
				13	110.0002860416817
				15	110.0002860416818
1	0.7	16	20		272.0002233160454
				1-14	271.3000000000000*
				15	271.6219989276613
				18	272.0002233160452
2	1.0	12	15		156.0007432191651
				1-9	155.0000000000000*
				10	155.4101468398408
				13	156.0007432191644
				15	156.0007432191651
3	0.7	10	12		110.0004230273525
				1-6	109.3000000000000*
				8	110.0003141668453
				10	110.0004230273523
5	1.0	20	20		420.0002449100770
				1-14	419.0000000000000*
				15	419.3717170996393
				18	420.0002449100768
				20	420.0002449100769

[a]The notation 1-9 indicates that the value of N_L ranges from one through nine.

[b]Asterisks indicate persistent lower bound.

CHAPTER VII

LOWER BOUNDS TO THE GROUND STATE ENERGY LEVELS OF TWO-ELECTRON IONS

The non-relativistic Hamiltonian of this system is divided into two parts:

$$\mathcal{H} = \mathcal{H}^0 + V \tag{7.1}$$

with

$$\mathcal{H}^0 = -\tfrac{1}{2}\Delta_1 - \tfrac{1}{2}\Delta_2 - \frac{Z}{r_1} - \frac{Z}{r_2} \tag{7.2}$$

and $$V = \frac{1}{r_{12}} \quad \text{in atomic units,}$$

where r_1 and r_2 denote the radial positions of electrons 1 and 2; r_{12} denotes the distance between electron 1 and 2; and Δ_i is the Laplacian operator in the coordinates $\vec{r}_i (i = 1,2)$. Since we estimate only the ground state which is singlet S, we restrict ourselves to the subspace in which the spacial coordinates r_1 and r_2 are symmetric with respect to their interchange, and the angular momentum is zero[21].

In the application of the method developed in Chapter V, we have freedom in choosing a subspace for the inner projection of the reaction operator $t(\mathcal{E})$. However, we have to take into account two factors in our consideration: one is the convenience of our treatment and the other is the convergence property of our lower bounds. Here we introduce two types of spaces for our inner projection: one is the

practically convenient Bazley space $\mathfrak{h}$, the other is the Löwdin space $\mathfrak{f}$. Since the choice of the Bazley space has some interesting features in connection with the simplicity of our calculations and the independence of our lower bound to the upper bound ε_0, we will briefly describe this choice in Appendix II, while in this chapter we will mainly work with the Löwdin space.

The Löwdin projection of t gives

$$t' = (\varepsilon_0 - \mathcal{H}^0)|\mathfrak{f}\rangle\Delta^{-1}\langle\mathfrak{f}|(\varepsilon_0 - \mathcal{H}^0) \tag{7.3}$$

where, using (4.22) and (5.67), Δ has the form

$$\Delta = \langle\mathfrak{f}|(\varepsilon_0 - \mathcal{H}^0)V^{-1}(\varepsilon_0 - \mathcal{H}^0) - (\varepsilon_0 - \mathcal{H}^0) + (\varepsilon_0 - \mathcal{H}^0)\Theta|\mathfrak{f}\rangle. \tag{7.4}$$

The unperturbed Hamiltonian $\mathcal{H}^0$ has known eigenvalues and eigenfunctions which are products of hydrogen-like wave functions. The discrete eigenvalues in atomic units are given by

$$-\frac{Z^2}{2}\left(\frac{1}{n^2} + \frac{1}{m^2}\right), \quad (n,m = 1,2,\ldots) \quad . \tag{7.5}$$

Arranging these in a non-decreasing sequence

$$E_1^0 \leq E_2^0 \leq \ldots, \tag{7.6}$$

one obtains from (7.5)

$$E_1^0 = -Z^2, \qquad E_2^0 = -0.625Z^2, \qquad E_3^0 = -\frac{5}{9}Z^2,$$

$$E_4^0 = -0.53125Z^2, \quad E_5^0 = -0.52Z^2 \qquad \ldots \quad . \tag{7.7}$$

Hence, if an upper bound to the ground state energy E_1 lies below $-0.625Z^2$, then the one-dimensional reference manifold can be used.

In Table 3 it is seen that, except for the case Z = 1, we can use (3.35) for the lower bound calculations of two-electron ions. The following six eigenfunctions of $\mathcal{H}^o$ are used for the multi-dimensional reference manifold:

$$\Psi_1^o = (\frac{1}{4\pi})R_{10}(r_1)R_{10}(r_2)$$

$$\Psi_i^o = (\frac{1}{4\pi\sqrt{2}})[R_{10}(r_1)R_{10}(r_2) + R_{10}(r_1)R_{10}(r_2)], \quad (i=2,3,4),$$

$$\Psi_5^o = (\frac{\sqrt{3}}{4\pi})[R_{21}(r_1)R_{21}(r_2)P_1(\cos\theta_{12})] \quad ,$$

$$\Psi_6^o = (\frac{\sqrt{5}}{4\pi})[R_{32}(r_1)R_{21}(r_2)P_2(\cos\theta_{12})] \quad , \qquad (7.8)$$

where $R_{n\ell}$ are hydrogenic normalized radial wave functions.

Six terms of the Hylleraas series[23] are used for the Löwdin space. The normalized forms of these six terms are:

$$j_1 = \frac{(2\eta)^3}{8\pi} e^{-\eta s} \quad , \qquad j_2 = \frac{(2\eta)^4}{16\pi\sqrt{6}} u e^{-\eta s} \quad ,$$

$$j_3 = \frac{(2\eta)^5}{96\pi} t^2 e^{-\eta s} \quad , \qquad j_4 = \frac{(2\eta)^4}{8\pi\sqrt{42}} s e^{-\eta s} \qquad (7.9)$$

$$j_5 = \frac{(2\eta)^5}{96\pi} s^2 e^{-\eta s} \quad , \qquad j_6 = \frac{(2\eta)^5}{160\pi\sqrt{3}} u^2 e^{-\eta s} \quad ,$$

where

$$s = r_1 + r_2, \quad t = r_1 - r_2 \quad \text{and} \quad u = r_{12} \quad . \qquad (7.10)$$

One can enlarge the Löwdin space in order to improve the lower bounds.

TABLE 3

E_2^o and E_U

Z	1	2	3	4	5	6	7	8	9	10
E_2^o	-0.625	-2.500	-5.625	-10.00	-15.625	-22.50	-30.625	-40.	-50.625	-62.5
E_U [a]	-0.52775	-2.90372	-7.27991	-13.65556	-22.03097	-32.40624	-44.78144	-59.15659	-75.53171	-93.90680

[a]The upper bounds (E_U) are given by Pekeris[22] using a determinant of order 203.

The arbitrary scaling parameter η is varied to maximize the lower bounds obtainable.

It is seen from (7.7) and Table 3 that for $T_o(\mathcal{E}_o)$ to be negative definite $S(\mathcal{O})$ has to contain at least four lower lying eigenfunctions of $\mathcal{H}^o$, namely Ψ_1^o, Ψ_2^o, Ψ_3^o and Ψ_4^o for $Z = 1$, whereas only one eigenfunction Ψ_1^o is sufficient for $Z \geq 2$. If one uses, as a typical example, all six functions in (7.8) for $S(\mathcal{O})$, then from (7.3) and (7.4) one obtains

$$\Delta = \langle \mathcal{J} | (\mathcal{E}_o - \mathcal{H}^o) V^{-1} (\mathcal{E}_o - \mathcal{H}^o) - (\mathcal{E}_o - \mathcal{H}^o) + \sum_{i=1}^{6} (\mathcal{E}_o - E_i^o) | \Psi_i^o \rangle \langle \Psi_i^o | \mathcal{J} \rangle , \tag{7.11}$$

and

$$t'_{k\ell} = \langle \Psi_k^o | (\mathcal{E}_o - E_k^o) | \mathcal{J} \rangle \Delta^{-1} \langle \mathcal{J} | (\mathcal{E}_o - E_\ell^o) | \Psi_\ell^o \rangle ,$$

where $$t'_{k\ell} = \langle \Psi_k^o | t' | \Psi_\ell^o \rangle . \tag{7.12}$$

Substituting (7.12) into (5.84), then the lowest eigenvalue of (5.84) is a lower bound to the ground state of $\mathcal{H}$. Once the Δ matrix is obtained the rest of the calculation is elementary. Most of the overlap integrals of the type $\langle \Psi_i^o | j_k \rangle$ are complicated in their algebraic form. Some typical examples of the terms which comprise each element of the Δ matrix are

$$\langle j_2 | (\mathcal{E}_o - \mathcal{H}^o) V^{-1} (\mathcal{E}_o - \mathcal{H}^o) | j_2 \rangle = \frac{3.28125(\mathcal{E}_o + \eta^2)^2}{\eta} - \frac{35}{24}(\mathcal{E}_o + \eta^2)\,\eta$$
$$+ 8.75(\mathcal{E}_o + \eta^2)(Z - \eta) + (4\ \ell n\ 2 - 4.5)\eta^2(Z - \eta)$$
$$+ \frac{1}{12}(48\ \ell n\ 2 - 29)\eta^3 + (6\ \ell n\ 2 + 4.5)\eta(Z - \eta)^2 \quad ,$$

$$\langle j_2 (\mathcal{E}_o - \mathcal{H}^o) | j_2 \rangle = (\mathcal{E} + \eta^2) - \frac{1}{6}\eta^2 + 1.5\eta(Z - \eta) \quad ,$$

$$\langle \Psi_2^o | j_1 \rangle = 512 \left[\frac{z\eta}{(z+\eta)(z+2\eta)}\right]^3 \left[\frac{\eta - z}{z + 2\eta}\right] ,$$

$$\langle \Psi_4^o | j_6 \rangle = \frac{\sqrt{6} z^3 \eta^5}{5} \left[\frac{32}{\alpha^3\beta^3}\left(\frac{1}{\alpha^2} + \frac{1}{\beta^2}\right) - \frac{24z}{\alpha^4\beta^3}\left(\frac{3}{\beta^2} + \frac{5}{\alpha^2}\right)\right.$$

$$\left. + \frac{24z^2}{\alpha^5\beta^3}\left(\frac{2}{\beta^2} + \frac{5}{\alpha^2}\right) - \frac{5z^3}{\alpha^5\beta^3}\left(\frac{2}{\beta^2} + \frac{7}{\alpha^2}\right)\right] ,$$

where $\alpha = \frac{z}{4} + \eta$ and $\beta = z + \eta$.

Numerical Results and Discussion

The numerical calculations was carried out on the IBM 709 electronic computer at the University of Florida Computing Center. In the estimation of the lower bound to the ground state energy, by use of (5.83), Givens[*9] subroutine was used.

The upper bounds, denoted by E_U, are taken from Table 3 and the lower bounds, denoted by E_L, are optimized with respect to the scaling parameter η. It can be seen that the scaling of the exponential coefficient for the reference function does not introduce any new feature in our problem. In the following tables, N_R denotes the dimension of the reference manifold associated with the eigenfunctions $\mathcal{H}^o$, $\Psi_1^o, \Psi_2^o, \ldots, \Psi_{N_R}^o$, whereas N_P denotes the dimension of the Löwdin space, $j_1, j_2, \ldots, j_{N_P}$. The energy is expressed in atomic units.

In Table 4, the lower bounds to the ground states of two electron ions from Z = 1 to Z = 10 are listed. The upper and lower bounds agree up to two significant digits except for Z = 1.

TABLE 4

UPPER AND LOWER BOUNDS TO THE GROUND STATE OF TWO-ELECTRON IONS

Z	E_U	E_L	$E_U - E_L$	Optimum η	Experiment [a]
1	-0.52775	-0.55593	0.0282	0.662	-0.529 ± 0.004
2	-2.9037	-2.9095	0.0058	1.73	-2.9037 ± 0.0001
3	-7.2799	-7.2938	0.0139	2.70	-7.2799 ± 0.0002
4	-13.655	-13.678	0.023	3.70	-13.655 ± 0.001
5	-22.031	-22.063	0.032	4.68	-22.031 ± 0.001
6	-32.406	-32.447	0.041	5.68	-32.406 ± 0.002
7	-44.781	-44.832	0.051	6.66	-44.781 ± 0.003
8	-59.156	-59.217	0.061	7.66	-59.156 ± 0.003
9	-75.531	-75.601	0.070	8.64	-75.530 ± 0.004
10	-93.906	-93.986	0.080	9.64	

[a] Except for Z = 1, the experimental values were evaluated from the ionization potential taken from [25] and for Z = 1 the ionization potential was taken from [24]. Corrections for mass-polarization, relativistic effect, and the Lamb shift were made using the Pekeris results [22] for 203 term wave functions.

In Table 5, the effects of N_R and N_P on the lower bounds for each Z are demonstrated with optimized η at $N_R = 6$ and $N_P = 6$. It is seen form Table 5 that the lower bounds do not improve, as one might hope from the discussion of Chapter V, when one increases the value of N_R. This might indicate that even if the lower bound $\mathcal{E}_1$ in (5.78) should be improved by increasing N_R, the corresponding improvement in $\mathcal{E}_1''$ may be offset to some extent by the tendency for $\mathcal{E}_1''$ to be depressed as the size of its secular equation increases (according to the variation principle). On the other hand the increased value of N_P gives rise to an improvement of the lower bounds. For Z = 1, the most outstanding change comes as we increase N_P from 3 to 4, which corresponds to adding j_4 to the Löwdin space spanned by j_1, j_2 and j_3, whereas for $Z \geq 2$ more than 50 percent of total improvement, from $N_{P=1}$ to $N_{P=6}$, takes place at the change of N_P from 2 to 3. Hence the choice of the proper function, rather than increasing the number of functions, for the Löwdin space seems to be more significant in our problem. The effect of the scaling parameter η on the lower bounds for Z = 1 (with $N_P = 4, 5,$ and 6) and Z = 2 (with $N_P = 1,2,\ldots 6$) is illustrated in Figs. 2 and 3. In both figures, the increase of N_R up to 6 does not improve lower bounds appreciably. For some part of the curves the improvement of the lower bounds by the increase of N_P is too small to be seen in the present figures. As a numerical demonstration, for Z = 1, η = 0.7 one has

N_P \ N_R	4	6
4	-0.5561906	-0.5561905
5	-0.5560375	-0.5560366
6	-0.5560233	-0.5560211

TABLE 5

EFFECT OF N_R AND N_P ON LOWER BOUNDS

N_R \ N_P	1	2	3	4	5	6
	Z = 1		E_U = -0.52775		η = 0.662	
4	-0.69296	-0.68528	-0.66914	-0.56474	-0.55594	-0.55594
5	-0.69296	-0.68505	-0.66886	-0.56467	-0.55594	-0.55593
6	-0.69296	-0.68505	-0.66886	-0.56467	-0.55594	-0.55593
	Z = 2		E_U = -2.9037		η = 1.72	
1	-3.1979	-3.1694	-2.9369	-2.9219	-2.9191	-2.9098
2	-3.1956	-3.1661	-2.9343	-2.9212	-2.9184	-2.9095
3	-3.1955	-3.1655	-2.9341	-2.9211	-2.9183	-2.9095
4	-3.1955	-3.1652	-2.9340	-2.9211	-2.9183	-2.9095
5	-3.1955	-3.1652	-2.9340	-2.9210	-2.9183	-2.9095
6	-3.1955	-3.1652	-2.9340	-2.9210	-2.9183	-2.9095
	Z = 3		E_U = -7.2799		η = 2.70	
1	-7.7895	-7.7410	-7.3760	-7.3211	-7.3155	-7.2941
2	-7.7879	-7.7379	-7.3732	-7.3205	-7.3148	-7.2938
3	-7.7876	-7.7374	-7.3729	-7.3204	-7.3147	-7.2938
4	-7.7875	-7.7372	-7.3727	-7.3204	-7.3147	-7.2938
5	-7.7875	-7.7371	-7.3727	-7.3204	-7.3147	-7.2938
6	-7.7875	-7.7371	-7.3727	-7.3204	-7.3147	-7.2938

TABLE 5(Continued)

	Z = 6		E_U = -32.406		η = 5.68	
1	-33.574	-33.472	-32.726	-32.518	-32.505	-32.448
2	-33.573	-33.470	-32.724	-32.518	-32.505	-32.447
3	-33.573	-33.470	-32.724	-32.518	-32.505	-32.447
4	-33.573	-33.470	-32.724	-32.518	-32.505	-32.447
5	-33.573	-33.470	-32.724	-32.518	-32.505	-32.447
6	-33.573	-33.470	-32.724	-32.518	-32.505	-32.447
	Z = 10		E_U = -33.906		η = 9.64	
1	-96.148	-96.027	-94.673	-94.117	-94.097	-93.986
2	-96.147	-96.026	-94.671	-94.116	-94.094	-93.986
3	-96.147	-96.026	-94.671	-94.116	-94.094	-93.986
4	-96.147	-96.026	-94.671	-94.116	-94.094	-93.986
5	-96.147	-96.026	-94.671	-94.116	-94.094	-93.986
6	-96.147	-96.026	-94.671	-94.116	-94.094	-93.986

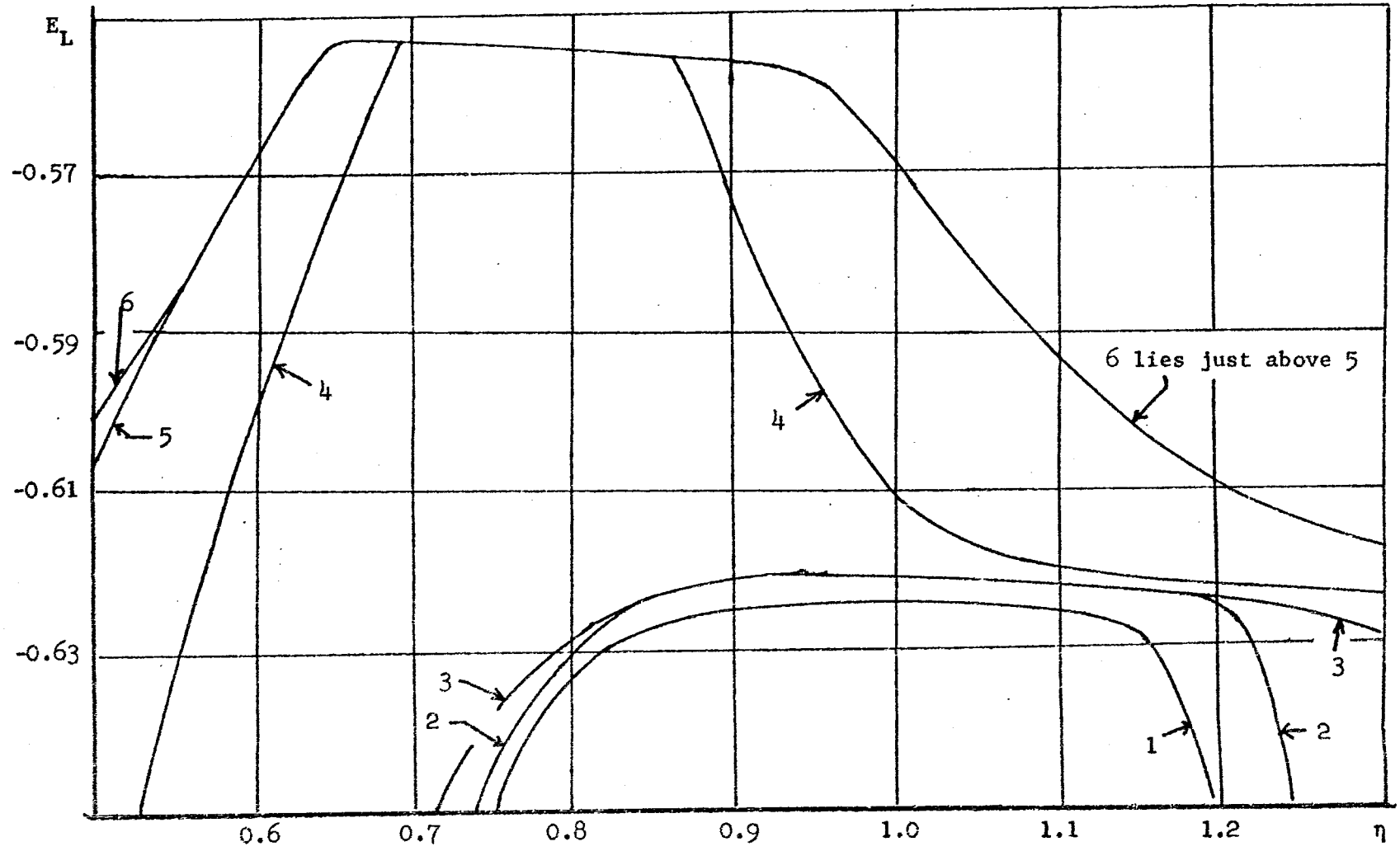

Fig. 2. Lower bounds (E_L) to the ground state of H^- as a function of a scaling parameter (η) with N_R=4. The number attached to each curve denotes the value of N_P.

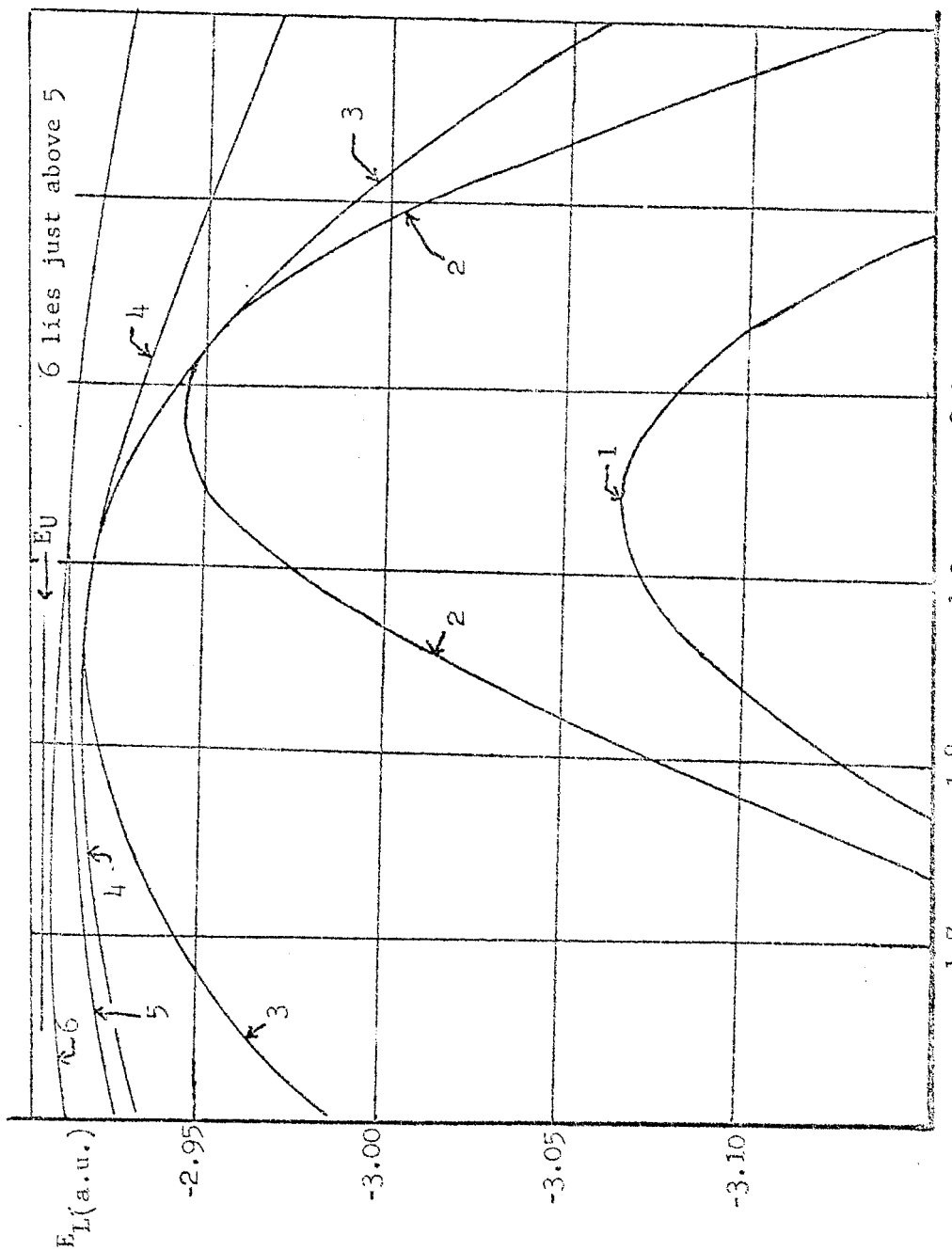

Fig. 3. Lower bound to the ground state of helium as a function of scaling parameter with N_R=1. The number associated to each curve denotes the value of N_P.

For H^-, the lower bounds assume a flat top type curve. The flat top behavior of the curves for Z = 1 may explain the large gap between the upper and the lower bounds. This behavior may indicate that the functions we have chosen for the Löwdin space, although suitable for helium, are probably not entirely suitable for H^- with respect to the variation of η.

A good choice of the Löwdin space is essential in order to improve our lower bounds. In contrast with the behavior for Z = 1, Fig. 3, for Z = 2, shows a fairly good convergence of the bound as we increase N_p; furthermore, the curves are of an approximately parabolic appearance indicating that the choice of the Löwdin space is satisfactory with respect to the variation of the scaling parameter η. Interestingly enough, Fig. 3 is very similar to that obtained by J. G. Gay[15]. He obtained the lower bound to the ground state of helium by solving the determinant:

$$\det \{ \langle \mathcal{J} | (E-\mathcal{H}^0)V^{-1}(E-\mathcal{H}^0) - (E-\mathcal{H}^0) | \mathcal{J} \rangle \} = 0. \qquad (7.13)$$

The comparison is made in Table 6 between the lower bounds obtained from (7.13) by Gay[15] and those obtained from (5.84). It is seen from Table 6 that the lower bounds obtained as eigenvalues of the intermediate Hamiltonian are slightly better than those obtained by the present method, but the differences in the lower bounds of those two methods decrease as one increases the value of N_p until at $N_p = 6$ there is essentially no difference. The dependence of the lower bounds on the scaling parameter η for Z = 4, 6, 8 and 10 is shown in Fig. 4, where N_R and N_p are fixed at the value of 6. As in the case of Z = 2, all curves are roughly parabolic.

TABLE 6

COMPARISON OF THE LOWER BOUND ENERGIES OF PRESENT METHOD FOR HELIUM WITH THOSE OBTAINED FROM EIGENVALUE PROBLEM OF THE INTERMEDIATE HAMILTONIAN

N_p	Method of Gay		Present Method		energy difference
	lower bound	optimum η	lower bound	optimum η	
1	-3.0657	1.93	-3.0690 (N_R=1) -3.0689 (N_R=6)	1.93	0.0033 0.0032
2	-2.9437	1.78	-2.9468 (N_R=1) -2.9465 (N_R=6)	1.97	0.0031 0.0028
3	-2.9208	1.85	-2.9220 (N_R=1) -2.9213 (N_R=6)	1.84	0.0012 0.0005
6	-2.9094	1.72	-2.9098 (N_R=1) -2.9095 (N_R=6)	1.73	0.0004 0.0001

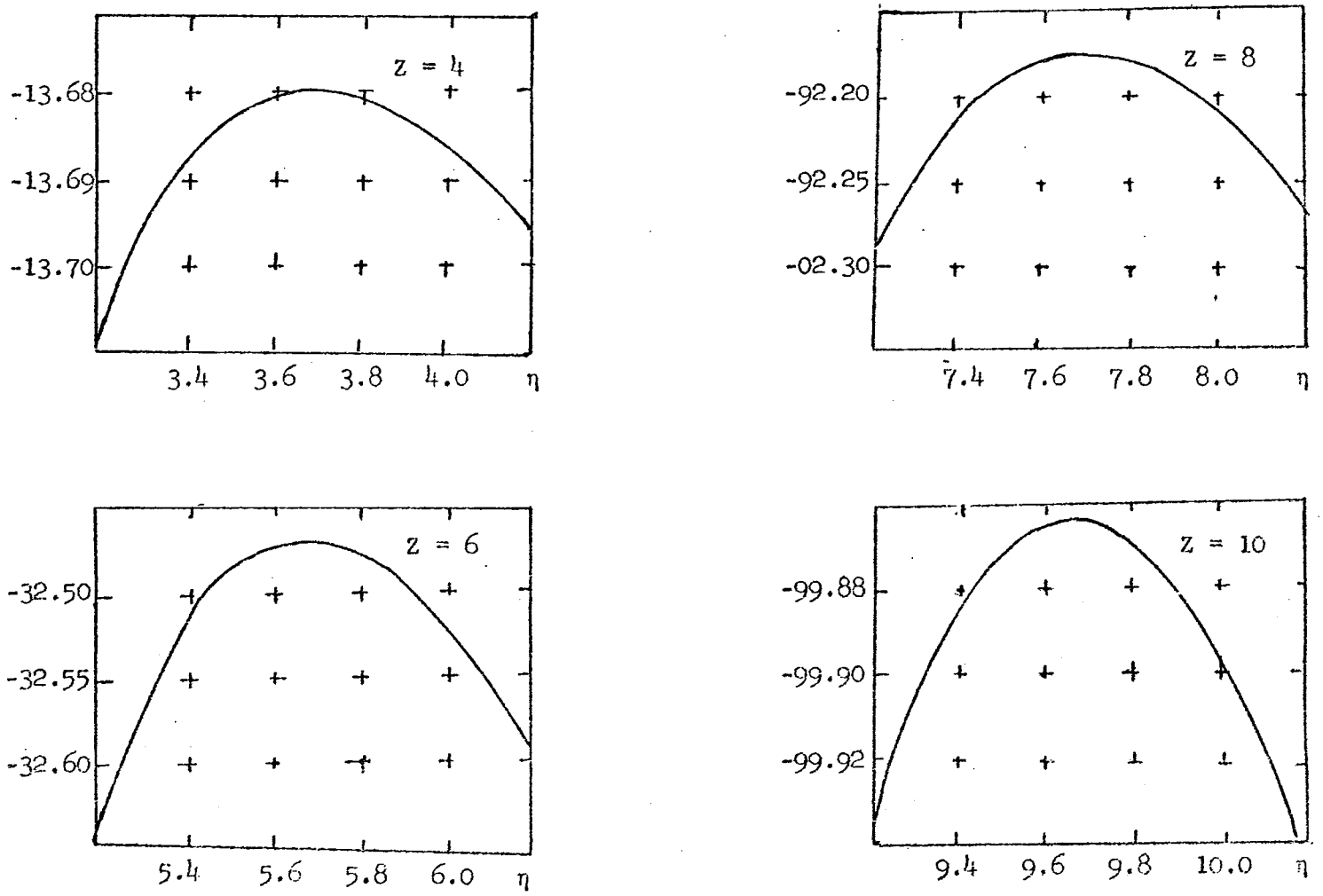

Fig. 4. The lower bound to the ground state of two electron ions for Z = 4, 6, 8, and 10 as a function of η at N_P=6 and N_R=6.

The upper bound of the H^- is improved[26] by 0.00115 a.u., from -0.52531 to -0.52646, by extending the Hylleraas-type wave function from three terms to six terms, whereas is seen from Table 5 the corresponding improvement for the lower bound is about 0.113. This shows that the lower bounds improve more rapidly than the upper bounds do by introducing more terms*12. Hence one can hope to improve the lower bounds of the ground state of H^- by introducing carefully chosen functions in the Löwdin space.

In concluding the discussion it can be noted that, as one can see from Fig. 2, the most outstanding improvement of the lower bound to the ground state of H^- takes place when one incorporates the function j_4 into the Löwdin space. The introduction of the function j_5 also shows remarkable improvement on the lower bound even if it does not render significant contribution between the range $\eta = 0.68$ and $\eta = 0.84$. In terms of hydrogenic radial functions, j_4 and j_5 assume the form

$$j_4 = N_4[R_{10}(r_1)R_{21}(r_2) + R_{21}(r_1)R_{10}(r_2)], \tag{7.14}$$

$$j_5 = N_5[R_{10}(r_1)R_{32}(r_2) + 2\, R_{21}(r_1)2\, R_{21}(r_2) + R_{32}(r_2)R_{10}(r_1)], \tag{7.15}$$

where N_4 and N_5 are normalization constants, showing that j_4 and j_5 are independent of θ_{12}, the angle between electron 1 and 2. Since $R_{10}(r)$, $R_{21}(r)$, and $R_{32}(r)$ have different spacial distributions from one another, it seems that the introduction of some functions, which can give a more flexible radial distribution with respect to the variation

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*12 See Table 1 of [15].

of over the wide range of space, can improve the lower bound satisfactorily. In this connection, it might be wothwhile to incorporate into the Löwdin space some carefully chosen radial functions which have two different orbital exponents, for example, a function of the form investigated by Chandrasekar[27],

$$j = (e^{-ar_1-br_2} + e^{-br_1-ar_2})(1 + c\cdot r_{12} + \cdots) \quad . \qquad (7.16)$$

It may be also worthwhile trying to use Hylleraas series given in (7.9) by giving a different scaling parameter for each function.

For practical applications, a proper choice of the functions with suitable scaling parameters for the inner projection is to be preferred over expanding the number of functions.

APPENDIX I

Evaluation of the Matrix Elements used in Chapter VII

For S-state configurations, the atomic wave function can be described in terms of the three coordinates[23].

$$\begin{aligned} s &= r_1 + r_2 \ , \\ t &= r_1 - r_2 \ , \\ u &= r_{12} \ . \end{aligned} \tag{A1.1}$$

The volume element in terms of s, t, u coordinates (Hylleraas coordinates) is [28,p.1737]

$$dv_1 dv_2 = \pi^2 u(s^2-t^2)\, du\, ds\, dt \tag{A1.2}$$

with the range

$$-u \leq t \leq u, \qquad 0 \leq u \leq s \leq \infty. \tag{A1.3}$$

In terms of the Hylleraas coordinates, $\mathcal{H}^0$ given by (7.2) assumes the form[29]

$$\mathcal{H}^0 = -\left[\frac{\partial^2}{\partial s^2} + \frac{\partial^2}{\partial t^2} + \frac{\partial^2}{\partial u^2} + \frac{2s(u^2-t^2)}{u(s^2-t^2)}\frac{\partial^2}{\partial s \partial u} + \frac{2t(s^2-u^2)}{u(s^2-t^2)}\frac{\partial^2}{\partial t \partial u} + \frac{4s}{(s^2-t^2)}\frac{\partial}{\partial s} - \frac{4t}{(s^2-t^2)}\frac{\partial}{\partial t} + \frac{2}{u}\frac{\partial}{\partial u} + \frac{4Zs}{(s^2-t^2)}\right] , \tag{A1.4}$$

and

$$V = \frac{1}{r_{12}} = \frac{1}{u} \ . \tag{A1.5}$$

The multi-dimensional reference functions in (7.8) are linear combinations of the form

$$f = e^{-as}\, e^{-bt}\, s^k\, t^\ell\, u^m \ , \tag{A1.6}$$

where $a>|b|>0$ and ℓ is even; whereas the function for the inner projection have the form

$$j = e^{-\alpha s} s^k t^{2\ell} u^m. \tag{A1.7}$$

Matrix elements involving functions of type f and j were all evaluated in a closed form. In the evaluation of Δ matrix using Hylleraas coordinates s, t and u, two types of integrals are utilized. One is

$$(\alpha/n,k,\ell,m) \equiv \int_o^\infty e^{-\alpha s} s^k ds \int_o^s u^m du \int_o^u (s^2-t^2)^n \, t^{2\ell} dt, \tag{A1.8}$$

where $n = -1,0,1$, $k \geq 0$, $\ell \geq 0$, $m \geq -1$ and $\alpha > 0$. The algebraic expressions for (A1.8) are given in[30]. The other is

$$\begin{aligned}(a,b/k,\ell,m) = & \int_o^\infty e^{-as} s^k ds \int_o^s u^m du \int_{-u}^u (s^2-t^2)\, t^\ell e^{-bt}\, dt \\ = & \frac{\ell!}{b^{\ell+m+2}} \sum_{p=0}^{\ell} \frac{(p+m)!}{p!} \sum_{q=0}^{p+m} \frac{(q+k)!}{q!} b^q \left[\frac{1}{(a+b)^{q+k+1}} \left\{ \frac{(q+k+2)(q+k+1)}{(a+b)^2} \right.\right. \\ & \left. - \frac{(\ell+2)(\ell+1)}{b^2} \right\} + \frac{(-1)^{m+q}}{(a-b)^{q+k+1}} \left\{ \frac{(q+k+2)(q+k+1)}{(a-b)^2} - \frac{(\ell+2)(\ell+1)}{b^2} \right\} \Bigg] \\ & - \frac{(\ell+2)!}{b^{\ell+m+4}} \sum_{p=\ell+1}^{\ell+2} \frac{(p+m)!}{p!} \sum_{q=0}^{p+m} \frac{(q+k)!}{q!} b^q \left\{ \frac{1}{(a+b)^{q+k+1}} \right. \\ & \left. + \frac{(-1)^{m+q}}{(a-b)^{q+k+1}} \right\} + \left\{ 1 + (-1)^m \right\} \frac{\ell!\, k!}{b^{\ell+m+2} a^{k+1}} \left[\left\{ \frac{(\ell+2)(\ell+1)}{b^2} \right.\right. \\ & \left. \left. - \frac{(k+2)(k+1)}{a^2} \right\} \left\{ \sum_{p=0}^{\ell} \frac{(p+m)!}{p!} \right\} + \frac{(\ell+m+1)!(2\ell+m+4)}{b^2\, \ell!} \right] . \end{aligned} \tag{A1.9}$$

The integral (A1.9) was used as a means of checking some algebraic expressions for the Δ matrix which were obtained by use of the polar coordinates[31].

For the convenience of Fortran programming this form is transformed into

$$(a,b/k,\ell,m) = \frac{\ell!}{b^{\ell+m+2}} \sum_{p=0}^{\ell} \frac{(p+m)!}{p!} \sum_{q=0}^{m} \frac{(q+k)!\,b^q}{q!} \left[\frac{1}{(a+b)^{q+k+1}} \left\{ \frac{(q+k+2)(q+k+1)}{(a+b)^2} - \frac{(\ell+2)(\ell+1)}{b^2} \right\} + \frac{(-1)^{m+q}}{(a-b)^{q+k+1}} \left\{ \frac{(q+k+2)(q+k+1)}{(a-b)^2} - \frac{(\ell+2)(\ell+1)}{b^2} \right\} \right]$$

$$+ \frac{\ell!}{b^{\ell+m+2}} \sum_{q=m+2}^{\ell+m} \frac{(q+k)!\,b^q}{q!} \sum_{p=q-m}^{\ell} \frac{(p+m)!}{p!} \left[\frac{1}{(a+b)^{q+k+1}} \left\{ \frac{(q+k+2)(q+k+1)}{(a+b)^2} - \frac{(\ell+2)(\ell+1)}{b^2} \right\} + \frac{(-1)^{m+q}}{(a-b)^{q+k+1}} \left\{ \frac{(q+k+2)(q+k+1)}{(a-b)^2} - \frac{(\ell+2)(\ell+1)}{b^2} \right\} \right] - \frac{(\ell+m+1)(2\ell+m+4)}{b^{\ell+m+4}} \sum_{q=0}^{\ell+m+1} \frac{(q+k)!\,b^q}{q!} \left[\frac{1}{(a+b)^{q+k+1}} + \frac{(-1)^{m+q}}{(a-b)^{q+k+1}} \right]$$

$$- \frac{(\ell+k+m+2)!}{b^2} \left[\frac{1}{(a+b)^{\ell+m+k+3}} + \frac{(-1)^{\ell}}{(a-b)^{\ell+m+k+3}} \right] + \left\{ 1 + (-1)^m \right\} \frac{k!}{b^{\ell+m+2} a^{k+1}} \left[\ell ! \sum_{p=0}^{\ell} \frac{(p+m)!}{p!} \left\{ \frac{(\ell+2)(\ell+1)}{b^2} - \frac{(k+2)(k+1)}{a^2} \right\} + \frac{(\ell+m+1)!\,(2\ell+m+4)}{b^2} \right] . \qquad \text{(A1.10)}$$

In order to avoid the effect of round-off error, (A1.9) is programmed in double precision. This Fortran Program is listed on the following pages.

```
      FUNCTION OHHIA,B,K,L,M)
C     FUNCTION DCT(M) AND DCTD(M,N) NEEDED
C     L, M, AND N MUST BE ZERO OR POSITIVE INTEGER.
C     B CANNOT BE ZERO. A IS POSITIVE. THE ABSOLUTE VALUE OF
C                                          B IS LESS THAN A.
      K1 = K+ 1
      K2 = K + 2
      L1 = L + 1
      L2 = L + 2
      M1 = M + 1
      M2 = M + 2
      LM = L + M
      KM = K + M
      LM1 = L + M + 1
      LM2 = L + M + 2
      LM4 = L + M + 4
      KM1 = K + M + 1
      KM2 = K + M + 2
      KLM2 = K + L + M + 2
      KLM3 = K + L + M + 3
      L2M4 = 2*L + M + 4
D     FK = K
D     FL = L
D     FM = M
D     FK1 = K1
D     FK2 = K2
D     FL1 = L1
D     FL2 = L2
D     FKM1 = KM1
D     FKM2 = KM2
D     FL2M4 = L2M4
D     ASQ = A*A
D     BSQ = B*B
D     AI = 1./A
D     BI = 1./B
D     AISQ = 1./ASQ
D     BISQ = 1./BSQ
D     APB = A + B
D     ANB = A - B
D     BPA = 1./APB
D     BNA = 1./ANB
D     APBSQ = APB*APB
D     ANBSQ = ANB*ANB
D     BPASQ = BPA*BPA
D     BNASQ = BNA*BNA
D     FLLB = ( (FL+2.)*(FL+1.) )/ BSQ
D     FKKA = ( (FK+2.)*(FK+1.) )/ASQ
    5 IF(L-(L/2)*2) 6, 6, 8
D   6 SIGL = 1.
    7 GO TO 9
D   8 SIGL = -1.
    9 IF( M-(M/2)*2 ) 10, 10, 12
D  10 SIGM = 1.
   11 GO TO 13
```

```
D   12 SIGM = -1.
D   13 RC1 = DCT(L)/(B**LM2)
D   14 Q = DCT(M)
    15 IF(L) 19, 19, 16
    16 DO 18 I=1,L
    17 IM = I + M
D   18 Q = Q + DCTD(IM,I)
D   19 RC2 = Q
D   20 RC3R = DCT(K)
D   21 RN1CR = BPA**K1
D   22 RN2CR = SIGM*(BNA**K1)
D   23 RN1NR = FK2*FK1*BPASQ
D   24 RN2NR = FK2*FK1*BNASQ
D   25 RN1R = RN1NR-FLLB
D   26 RN2R = RN2NR-FLLB
C      FUD IS THE PRODUCT ONLY FOR RUNNING INDEX, HERE START
                                                FROM RC3R.
D   27 FUD = RC3R*( RN1CR*RN1R + RN2CR*RN2R )
    28 IF(M) 39, 39, 29
    29 DO 38 I=1,M
D   30 FI = I
D   31 RC3R = RC3R*B*(FI+FK)/FI
D   32 RN1CR = RN1CR*BPA
D   33 RN2CR = - RN2CR*BNA
D   34 RN1NR = (FK2+FI)*(FK1+FI)*BPASQ
D   35 RN2NR = (FK2+FI)*(FK1+FI)*BNASQ
D   36 RN1R = RN1NR - FLLB
D   37 RN2R = RN2NR - FLLB
C      FUD IS RUNNING FROM  RC3R
D   38 FUD = FUD + RC3R*( RN1CR*RN1R + RN2CR*RN2R )
D   39 R = RC1*RC2*FUD
    40 IF(L) 41, 41, 43
D   41 S = 0.
    42 GO TO 65
D   43 SC1 = DCT(L)/(B**LM2)
D   44 SC2R = DCTD(KM,M)*(B**M)
D   45 SN1CR = BPA**KM1
D   46 SN2CR = BNA**KM1
D   47 FUD = 0.
    48 DO 63 I=M1,LM
D   49 FI = I
D      SC2R = SC2R*B*(FK+FI)/FI
D   51 Q = 0.
    52 INM = I-M
    53 DO 55 J=INM,L
    54 JM = J + M
D   55 Q = Q + DCTD(JM,J)
D   56 SC3R = Q
D   57 SN1CR = SN1CR*BPA
D   58 SN2CR = - SN2CR*BNA
D   59 SN1NR = (FK2+FI)*(FK1+FI)*BPASQ
D   60 SN2NR = (FK2+FI)*(FK1+FI)*BNASQ
D   61 SN1R = SN1NR - FLLB
D   62 SN2R = SN2NR - FLLB
```

```
C       FUD IS RUNNING FROM SC2
D    63 FUD = FUD + SC2R*SC3R*( SN1CR*SN1R + SN2CR*SN2R )
D    64 S = SC1*FUD
D    65 TC1 = DCT(LM1)*FL2M4*(BI**LM4)
D    66 TC2R = DCT(K)
D    67 TN1R= BPA**K1
D    68 TN2R = SIGM*(BNA**K1)
C       FUD IS RUNNING FROM TC2R
D    69 FUD = TC2R*( TN1R + TN2R )
     70 DO 75 I=1,LM1
D    71 FI = I
D    72 TC2R = TC2R*B*(FK+FI)/FI
D    73 TN1R = TN1R*BPA
D    74 TN2R = - TN2R*BNA
C       FUD IN RUNNING FROM TC2R.
D    75 FUD = FUD + TC2R*( TN1R + TN2R )
D    76 T = TC1*FUD
D    77 U = DCT(KLM2)*BISQ*( (BPA**KLM3) + SIGL*(BNA**KLM3) )
     78 IF( M-(M/2)*2 ) 79, 79, 89
D    79 VC1 = DCT(K)*(AI**K1)*(BI**LM2)*2.
D    80 Q = DCT(M)
     81 IF(L) 85, 85, 82
     82 DO 84 I=1,L
     83 IM = I + M
D    84 Q = Q + DCTD(IM,I)
D    85 VN1 = DCT(L)*Q*( FLLB-FKKA)
D    86 VN2 = DCT(LM1)*FL2M4*BISQ
D    87 V = VC1*( VN1+VN2 )
     88 GO TO 90
D    89 V = 0.
D    90 DHH = R + S - T - U + V
D    91 RETURN
        END
```

```
      FUNCTION DCT(M)
C     FUNCTION MAKING FACTORIALS.
    4 IF(M-1) 5, 5, 7
D   5 DCT = 1.
D   6 RETURN
    7 K = 1
    8 IF(M-8) 9, 9, 13
    9 DO 10 I=2,M
   10 K = K*I
D  11 DCT = K
D  12 RETURN
   13 DO 14 I=2,8
   14 K=K*I
D  15 S = K
   16 DO 18 I=9,M
D  17 FI = I
D  18 S = S*FI
D  19 DCT = S
D  20 RETURN
      END
```

```
      FUNCTION   DCTD(M,N)
C     FUNCTION MAKING M FACTORIAL DEVIDED BY N FACTORIAL.
C     M MUST BE LARGER OR EQUAL TO N.
C     M AND N MUST BE POAITIVE INCLUDING ZERO.
   10 N1 = N+1
   11 IF(M-N) 14, 12, 14
D  12 DCTD = 1.
D  13 RETURN
   14 IF(M) 15, 12, 15
D  15 S = 1.
   16 DO 18 I=N1, M
D  17 FI = I
D  18 S = S*FI
D  19 DCTD = S
D  20 RETURN
      END
```

APPENDIX II

Lower bounds using the Bazley Space

It was seen in Chapter V that for $V > 0$, one obtains

$$t^{-1} = V^{-1} - T_o \quad . \tag{A2.1}$$

If an upper bound $\mathcal{E}_o$ satisfies the relation

$$E_p^o < \mathcal{E}_o < E_{p+1}^o \quad , \tag{A2.2}$$

where E_p^o - the p^{th} eigenvalue of $\mathcal{H}^o$ from below, then $t(\mathcal{E}_o)$ becomes positive definite if one uses the projection operator defined in (5.76);

$$\mathcal{O} = \sum_{i=1}^{g} |\Psi_i^o\rangle\langle\Psi_i^o| \quad ; \tag{A2.3}$$

where $g \geq p$ and Ψ_i^o is an orthonormalized eigenfunction of $\mathcal{H}^o$ with the eigenvalue E_i^o. If the Bazley space is chosen by

$$\mathfrak{h} = \{\Psi_1^o, \Psi_2^o, \ldots \Psi_n^o\} \quad , \tag{A2.4}$$

then the corresponding form of (7.11) reads

$$\Delta_{ij} = \langle\Psi_i^o|V^{-1}|\Psi_j^o\rangle - \frac{\delta_{ij}}{\mathcal{E}_o - E_i^o} \quad \text{if } i > g \tag{A2.5}$$

or

$$\Delta_{ij} = \langle\Psi_i^o|V^{-1}|\Psi_j^o\rangle \qquad \text{if } i \leq g. \tag{A2.6}$$

This choice of the inner projection has an advantage in that it simplifies the calculations. For this case

$$t'_{k\ell} = (\Delta^{-1})_{k\ell} \tag{A2.7}$$

$$\mathcal{H}''_{k\ell} = E^o_k \delta_{k\ell} + (\Delta^{-1})_{k\ell} \quad . \tag{A2.8}$$

The lowest eigenvalue of the matrix obtained from (A2.8) gives a lower bound to the ground state energy of $\mathcal{H}$.

As a particular case, if we let n $\leq$ g, then every element of the Δ matrix has the form (A2.6) and the corresponding lower bound is independent of an upper bound $\mathcal{E}_o$.

The simplest example of this choice is rendered by the one-dimensional Bazley space

$$\mathbb{h} = \Psi^o_1 \quad , \tag{A2.9}$$

then

$$\Delta^{-1} = \langle \Psi^o_1 | V^{-1} | \Psi^o_1 \rangle^{-1} \quad , \tag{A2.10}$$

$$t'_{k\ell} = \langle \Psi^o_1 | V^{-1} | \Psi^o_1 \rangle^{-1} \delta_{k1} \delta_{\ell 1} \quad , \tag{A2.11}$$

$$\mathcal{H}''_{k\ell} = [E^o_k + \langle \Psi^o_1 | V^{-1} | \Psi^o_1 \rangle^{-1} \delta_{k1}] \delta_{k\ell} \quad .$$

A lower bound, for this case, is given by

$$E^o_1 + \langle \Psi^o_1 | V^{-1} | \Psi^o_1 \rangle^{-1} \quad \text{or} \quad E^o_2$$

which ever is lower.

For the two electron ions, one has

$$E^o_1 + \langle \Psi^o_1 | V^{-1} | \Psi^o_1 \rangle^{-1} = - Z^2 + \frac{16}{35} Z$$

and

$$E_o^{\,2} = -\frac{5}{8}Z^2 \quad .$$

It is seen that for $Z = 1$, E_2^o is a lower bound to the ground state energy whereas for $Z \geq 2$, $-Z^2 + \frac{16}{35}Z$ is a lower bound. It is shown[6] that $E_o^{\,1} + \langle \Psi_1^o | V^{-1} | \Psi_1^o \rangle^{-1}$ is a lower bound to the ground state energy of $\mathcal{H}$ if

$$E_1^o < \mathcal{E}_o < E_2^o$$

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